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PCT

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(54) Title: METHOD OF DEPOSITION

(57) Abstract

There is described a method of chemically depositing a substance. The method is of utility in the direct manufacture of in-
tegrated circuits and in the manufacture of a photomask for use in production of integrated circuits. The method involves the use
of a compound which degrades into a deposit and a residue when a radiant beam (e.g. a laser beam) or a particle beam (e.g. an
electron beam) is applied. The residue and any unreacted compound may be washed off the substrate to which it has been appli-
ed. Nanoscale dimensions of the deposit can be achieved. A particularly suitable organometallic compound is tetra-sec butyl di-
aurum difluoride.

1   "Method of Deposition"

2

3   This invention relates to a method of depositing

4   substances, for example metals. The method may be used

5   in the manufacture of integrated circuits and

6   photomasks.

7

8   Modern technological demands in integrated circuitry,

9   for example opto-electronics and electronic surgical

10   implants, now require methods by which ultra fine metal

11   lines of submicron dimensions can be deposited onto

12   inert substrate materials. There is a considerable

13   demand for submicron technology in a wide variety of

14   disciplines, but there are many difficulties in

15   developing nanoscale metal deposition processes by

16   conventional lithographic methods. Lithography is the

17   process by which a pattern is transferred to the

18   surface of a substrate material. Before this process

19   can occur a photomask has to be prepared which defines

20   the pattern ultimately to be achieved on the substrate

21   layer.

22

23   Conventionally the photomasks required in the

24   manufacture of integrated circuits are made by applying

25   a film layer of metal, usually chromium since this

1   resists scratching or etching and has good adhesion
2   properties, by metal vapour deposition to a highly pure
3   quartz substrate which has been polished to give an
4   extremely flat surface. The exposed metal is then
5   covered with electron beam resist (which is a material
6   that is sensitive to a beam of electrons and is
7   disrupted on exposure thereto) by placing a drop of
8   resist in the middle of a spinning disk of mask
9   material. The resist is then baked and dried in an
10   oven. The usual electron beam resist is
11   polybutylsulphone (PBS).
12.
13   An electron beam is directed at the resist face of the
14   resist/metal/substrate composite to degrade portions of
15   the resist, leaving unaffected a pattern required for
16   the integrated circuit. The degraded resist is then
17   dissolved away using a proprietary etchant to expose
18   the layer of metal in the areas where the resist has
19   been degraded, and this is subjected to wet etching by
20   ceric ammonium nitrate to remove the metal and expose
21   the quartz substrate. The remaining resist is then
22   burnt off from the residual metal, resulting in a
23   product through which light can pass apart from the
24   areas masked by metal.
25
26   The photomask thus produced is used to define a pattern
27   on a silicon chip coated with photoresist, by passing
28   ultraviolet light through the photomask to degrade the
29   photoresist in the defined areas.
30
31   This method of manufacturing photomasks has a number of
32   disadvantages. For example, the dissolution of the
33   degraded photoresist may not be entirely uniform, and
34   while the result is adequate for many products current
35   computer technology demands increasingly dense patterns

3

1   on integrated circuits and therefore higher-definition
2   photomasks, down to the nanoscale level.
3
4   A further area of loss of definition is the wet etch
5   process for removing the unwanted chromium. The etch
6   material attacks the upper, exposed face of the
7   chromium but as it penetrates into the chromium layer
8   its effect is not unidirectional, so instead of
9   producing vertical walls for the residual chromium it
10   erodes and undercuts these walls. This can produce a
11   scattering effect on the ultraviolet light during
12   manufacture of the integrated circuits, reducing
13   definition of the applied pattern. This is one of the
14   principal problems in mask-making.
15
16   Where several photomasks are used successively in the
17   manufacture of a chip, accurate registration of each
18   mask is absolutely essential so that each feature
19   appears in the correct place on the finished chip.
20   Problems in epitaxy can cause pattern shift and thus
21   registration. Usually registration is accurate to +/-
22   0.2μm. Registration problems, epitaxy growth problems,
23   undercutting, constructive and destructive interference
24   during lithographic process at micron and submicron
25   dimensions, all contrive to indicate that mask-making
26   at nanometer dimensions may require an entirely new
27   manufacturing process.
28
29   For nanoscale circuits, conventional methods using
30   metallic inks do not as yet possess the specifications
31   which can ensure the deposition of accurate straight
32   lines of high specification, and the formation of
33   perfect right angles rather than arcs during integrated
34   circuit manufacture. The low specification of the
35   conventional process of metallisation can result in

4

1   circuit overlap and circuit breakage which cannot be
2   tolerated when scribing nanoscale circuits. Further,
3   when ultra fine lines are required to carry current it
4   is a fundamental requirement that the circuit-integrity
5   remains intact, and hence conductive materials which
6   are oxidized are not ideally suited to operate at such
7   dimensions.
8
9   According to the present invention there is provided a
10   method of chemical deposition comprising applying to a
11   substrate a compound which degrades under the effect of
12   a radiant or particle beam to produce a deposit,
13   applying to selected surface areas of said compound
14   such a radiant or particle beam and removing the
15   degraded compound and the unaffected compound from the
16   substrate. The deposit is left upon the substrate.
17
18   The process of the present invention causes degradation
19   of the compound only where contacted by the radiant or
20   particle beam. In other words, the dimensions of the
21   deposit caused by degradation of the compound is
22   proportional to the focal width of the irradiating
23   beam. Nanoscale dimensions may be achieved by the
24   process of the present invention.
25
26   Where the compound degrades to form a deposit of a
27   metallic or other conductive substance, then the method
28   may be used to manufacture integrated circuits directly
29   on the substrate. The deposit is preferably a metal or
30   metal alloy, and mention may be made of metals such as
31   gold, tin and chromium, or the deposit may be a
32   conductive non-metal or semi-metal, such as germanium.
33
34   In a further aspect there is provided a method of
35   manufacture of an integrated circuit, said method

5

1   comprising applying to a substrate a compound which
2   degrades under the effect of a radiant or particle beam
3   to produce a conductive, preferably metallic deposit,
4   applying to selected surface areas of said compound
5   such a radiant or particle beam and removing the
6   degraded compound and the unaffected compound from the
7   substrate.
8
9   Alternatively, the method of the present invention may
10   be used to manufacture a photomask which is then
11   subsequently used in lithography to manufacture
12   integrated circuits. In this embodiment the substrate
13   should be translucent or transparent and the deposit
14   formed by degradation of the compound should be opaque.
15   The deposit provides a barrier to passage of
16   ultraviolet light during use of the photomask in making
17   integrated circuits, as with the chromium in
18   conventional photomasks.
19
20   Thus in a yet further aspect, the present invention
21   provides a method of manufacture of a photomask, said
22   method comprising applying to a transparent or
23   translucent substrate a compound which degrades under
24   the effect of a radiant or particle beam to produce an
25   opaque deposit, applying to selected surface areas of
26   said compound such a radiant or particle beam and
27   removing the degraded compound and the unaffected
28   compound from the substrate.
29
30   In this embodiment the deposit formed by the action of
31   the particle or radiant beam need only be opaque and
32   there is no requirement for the deposit to be
33   conductive. Therefore the deposit may be of any
34   suitable opaque material, whether metal or non-metal.
35   The opaque deposit may be for example a metal or semi-

1   metal such as gold, tin, germanium or chromium, an
2   alloy, or a non-metal such as silicon or carbon.
3
4   In the present invention, the compound may be heat-
5   sensitive so that the use of a radiant beam in the form
6   of a laser beam degrades the compound to produce the
7   deposit.
8
9   Preferably, however, the particle beam is an electron
10   beam, in which case the compound may be for example an
11   organometallic compound which degrades under the effect
12   of the beam to deposit a metal on the substrate.
13
14   Conventionally the steric properties of the
15   organometallic material which may be used as the
16   compound in the process of invention are optimised by
17   selecting d^8 configurations which give square planar
18   geometry in the organometallic compound. Such
19   compounds include organometallic gold, platinum or
20   palladium fluorides.
21
22   In a yet further aspect, the present invention provides
23   a gold organometallic fluoride. Optionally the gold
24   organometallic fluoride may be used in the method of
25   deposition described herein.
26
27   Gold is an especially useful metal for inclusion in an
28   organometallic compound to be used in the method of
29   this invention, and a suitable organometallic form is
30   di-sec butylaurum (III) fluoride dimer.
31
32   Gold chemistry exists mainly in the Au(I) and Au(III)
33   oxidation states. Inorganic gold compounds usually
34   have the linear 2 co-ordination state and occasionally
35   exist in trigonal planar or tetrahedral configurations.

7

1	Au(III) compounds are in general square planar but can
2	exist in five or six coordinated states. Simple
3	organogold compounds (AuR - where R is any organic
4	group) have not as yet been found although adduct
5	compounds of Au(I) with phosphines or isocyanides are
6	known. Trigonal planar Au(I) organoaurates (eg
7	Li[AuCH$_3$]$_2$) exhibit low stability, spontaneously
8	decomposing by reductive elimination of the methyl
9	groups to give ethane. The trigonal planar gold
10	complexes gain stability if complexed with larger
11	ligands (eg Li(PMDT)[AuCH$_3$)$_2$, where PMDT = pentamethyl-
12	diethylenetrisamine)
13	
14	Au(I) organyls are also accessible through carbene
15	insertion into the Au-Cl bond.
16	
17	eg (C$_2$H$_5$)$_3$PAuCl + CH$_2$N$_2$ -------) (C$_2$H$_5$)$_3$PAuCl + N$_2$
18	
19	Au(III) organyls also require additional ligation to
20	provide stability. Square planar compounds are
21	obtained eg: (C$_6$F$_5$)$_2$ AuClPPh$_3$). Halogen bridging Au
22	complexes are known through the auration reaction:
23	
24	eg: 2Au$_2$Cl$_6$ + 2C$_6$H$_5$ -----) C$_6$H$_5$.Cl.Au.Cl.Cl.Au.Cl.C$_6$H$_5$
25	
26	Other typical organometallic compounds for use in this
27	invention are polyalkyl metal fluorides, for example
28	polydibutyltin difluoride, as these compounds contain
29	generally linear chains which allow good definition of
30	the affected areas of the compound on application of
31	the radiant or particle beam.
32	
33	The organometallic compounds are advantageously
34	fluorides since the fluoride component enhances the
35	adhesion between the substrate (such as silicon or

1   quartz) and the metal film formed after irradiation.
2   The enhanced adhesive is believed to be due to the
3   formation of Si-F bonds. This enhanced adhesion is not
4   achieved with the equivalent chloride and bromide
5   compounds. Particularly good adhesion is observed when
6   tetra-sec-butyldiaurum difluoride is used as the
7   organometallic compound. A further advantage is that an
8   especially even dispersion of organometallic compound
9   is observed where a fluoride compound is used.
10
11 Fluorine bridging in organogold complexes has not been
12 reported but pentafluorochalchogenate derivatives of
13 gold are known (ie Au(OTeF$_5$)$_3$). The group OTeF$_5$ is often
14 regarded as a pseudohalogen but more precisely is a
15 pseudofluorine. The ability of Au to form bridging
16 species renders the gold pentafluorochalcogenate
17 compound the only known binary transition metal
18 derivative of OTeF$_5$. This compound is of a
19 centrosymmetric dimer with four terminal TeF$_5$ groups and
20 two u-oxo bridging bidentate OTeF$_5$ groups
21
22 Further according to the invention there is provided a
23 method of preparing polydibutyltin difluoride,
24 comprising fluorinating polydibutyltin dichloride.
25
26 Polydibutyltin dichloride is commercially available but
27 is unstable at ambient temperature. The difluoride,
28 while known, has until now been very difficult to
29 produce.
30
31 The fluorination may be carried out using for example
32 sodium fluoride, and the resulting polydibutyltin
33 difluoride may be used in the manufacture of photomasks
34 by applying it, for example by spinning, to a
35 transparent or translucent substrate such as quartz.

9

1   In this process the quartz is rapidly rotated while the
2   polydibutyltin difluoride in solution is slowly
3   applied, for example by drip, to it. The solvent is
4   then driven off leaving an accurately-controlled layer
5   of the organometallic compound.
6
7   In some cases it is possible to deposit the opaque
8   material by application to the substrate of a solution
9   of the degradable compound and then driving off the
10   solvent, preferably by microwave heating which has the
11   effect of allowing the solvent to be removed from the
12   substrate interface early in the procedure, thereby
13   producing effective adhesion between the deposited
14   degradable compound and the substrate.
15
16   In investigating the yield of organometallic precursor
17   material extracted from the reactant mixture as a
18   function of solvent polarity, cyclohexane, n-hexane,
19   isopentane, chlorofluorocarbon 113 (CCl_2FCClF_2), CFC-
20   113a (CCl_3CF_3), n-pentane and iso-pentane have been
21   examined. The optimum solvent to provide a smooth even
22   distribution of organometallic material on a quartz
23   substrate was found to be a low-boiling-point aliphatic
24   hydrocarbon solvent. Hence, n-pentane or isopentane
25   are excellent solvents for work to be performed at
26   ambient temperatures.
27
28   Embodiments of the present invention will now be
29   described by way of illustration in the following
30   Examples.
31
32
33

1   Example 1

2

3   Preparation of Polydibutyltin difluoride

4

5   Analar grade methanol (50ml, B.D.H.) was transferred to

6   a conical flask containing 2.1g of dried sodium

7   fluoride (Aldrich Chemical Co.,). The flask was shaken

8   to dissolve the solid material. Dibutyltin dichloride

9   (0.5g, Aldrich Chemical Co.,) was added and the conical

10   flask was stoppered and sealed using paraffin film.

11   The system was shaken for 1 hour, then allowed to stand

12   for 12 hours at ambient temperature.

13

14   The reaction mixture was then passed through a sintered

15   glass filter to remove any undissolved sodium fluoride

16   prior to the eluent being transferred to a phase

17   separation vessel. Petroleum ether (bp. 60-80°C, 100

18   ml) was added to the eluent phase and the reaction

19   mixture shaken before allowing the mixture to settle

20   and separate. Using the upper phase, the purification

21   process was repeated a further three times using

22   methanol (100ml) before the upper phase was finally

23   transferred to a 250 ml round bottom flask. The flask

24   containing the reaction solution was affixed to a

25   rotary evaporator and allowed to evaporate down until a

26   precipitate appeared.

27

28   The solution was analysed by Raman Spectroscopy and

29   identified as a low molecular weight polymer of

30   dibutyltin difluoride.

31

32   Application and Preparation of Organometallic Overlayer

33

34   The solution of polydibutyltin difluoride monomer

35   prepared above was spun onto a clean polished quartz

1   plate. As the solvent evaporated off a film of

2   polymeric dibutyltin difluoride formed on the quartz

3   substrate. The organometallic overlayer supported on

4   the quartz substrate was placed in a JEOL T300 Scanning

5   Electron Microscope and bombarded with electrons

6   (energy 30 keV) for a time which varied from 5s to 10

7   min over an area of 100 x 100 μm. of the organometallic

8   sample, then moved to an adjacent area.

9

10   After irradiation of each area the sample was examined

11   using an optical microscope to reveal a linear track of

12   metallic particles, approx. 10 μm wide. The non-

13   degraded polydibutyltin difluoride film was removed by

14   dissolution in methanol.

15

16   Using the method of this embodiment it is possible to

17   produce a photomask of very high definition so that

18   dense and discrete patterns can be applied to silicon

19   chips to provide integrated circuits. The method

20   removes the need for affected electron beam resist to

21   be dissolved as in the conventional method, and also

22   for the wet etch process, both of which reduce the

23   definition and performance of the photomask.

24

25   Example 2

26

27   Preparation of Di-sec butylaurum (III) Fluoride dimer.

28

29   Magnesium turnings were degreased by washing in sodium

30   dried ether and transferred to a double-necked round

31   bottom flask containing a magnetic stirring bar.

32   Sufficient sodium dried ether was added to cover the

33   magnesium turnings. The flask was fitted with a water

34   cooled condenser and a dropping funnel charged with

35   5.62g dibutyl bromide (Aldrich Chemical Co.) in 80ml of

1   sodium dried ether. The butylbromide/ ether mixture

2   was added slowly and allowed to react with stirring

3   with the magnesium turnings. The system was left to

4   react for 2 hours at ambient temperature.

5

6   The prepared butyl magnesium bromide/ether mixture was

7   decanted to a dry dropping vessel and fitted to a

8   double necked roundbottom flask containing an etheral

9   solution of aurum (III) chloride (500mg in 20ml ether

10 Aldrich Chemical Co) cooled with powdered ice. The

11 etheral solution of butyl magnesium bromide was added

12 slowly with stirring to the aurum (III) chloride

13 solution over a 20 minute period. After reaction

14 powdered ice was added to the reactant mixture which

15 was then allowed to warm up to ambient temperature.

16

17 The resultant organometallic gold halide was extracted

18 from the reactant mixture using isopentane in a phase

19 separation process. A dry methanol/isopentane phase

20 separation process was performed a further three times.

21 The product mixture was reacted with sodium fluoride

22 (Aldrich Chemical Co, 2.1g) dissolved in 50ml of dried

23 methanol (BDH), and shaken at ambient temperature over

24 a 24 hour period. The mixture was then passed through

25 a sintered glass filter to remove any undissolved NaF

26 prior to the eluent being transferred to a phase

27 separation vessel. Three phase separation cycles were

28 performed using an isopentane/dry methanol mixture

29 containing the reaction products, the hydrocarbon phase

30 being carried over in each step of the separations.

31 The final hydrocarbon phase was transferred to a round

32 bottom flask, affixed to a rotary exaporator, and

33 allowed to evaporate down until a precipitate appeared.

34 The product material had a white waxy appearance and

35 gave off a pungent odour. Contact of the product

1   material with the skin left a purple stain consistent

2   with the deposition of colloidal gold.

3

4   Characterisation of the product material was performed

5   using ^1H, ^{13}C, ^{19}F, and Distortionless Enhancement by

6   Polarization Transfer (DEPT) liquid phase NMR (nuclear

7   magnetic resonance) analysis using $CDCl_3$ or

8   deuterobenzene as solvent (Figures 1-5). Mass

9   spectroscopy was also used to identify the product

10   material (Figures 6-7).

11

12   Results:

13

14   ^1H NMR analysis of the product material gave peaks at

15   1.38 (hextet), 1.13 (hextet) and 0.79 (d of d) (Figures

16   1 and 1a). Two dimensional ^1H analysis of the material

17   shows three proton environments (Figure 2) and DEPT

18   analysis shows that the proton arrangement on the

19   organic liquid is one carbon containing an even number

20   of protons and three carbons containing an odd number

21   of protons (Figure 4). ^{13}C NMR analysis (Figure 3) of

22   the product material shows 4 peaks at 31.5, 29.7, 22.2,

23   11.7 ppm relative to TMS. The data indicates that four

24   carbon environments are present in the product

25   material. ^{19}F NMR analysis of the product material

26   (proton coupled and proton decoupled spectra) shows a

27   singlet peak at -66.3 ppm confirming the presence of

28   fluorine in the product. The ^{19}F NMR datum (Figure 5)

29   also indicates that the fluorine environment is

30   contained in a symmetrical field.

31

32   Mass spectroscopic analysis of the product material

33   confirms the molecular ion mass of the product material

34   to be 661 amu (Figures 6 and 7). Fragmentation of the

35   product material is consistent with the loss of the

1   following molecular fragments:-

2

3   <u>Fragments</u>   <u>Residual Mass</u> (amu)

4

5   CH_3- group   647

6

7   2 @ $CH-$ 632

8

9   3 @ CH_3- + 1 @ C_4H_9- 558

10

11   3 @ CH_3- + 1 @ C_3H_7- + 1 @ C_4H_9- 516

12

13   1 @ Au   463

14

15   1 @ Au + 1 @ C_3H_7- 421

16

17   1 @ Au + 1 @ C_3H_7- + 1 @ F   402

18

19   1 @ Au + 1 @ C_4H_9- + 1 @ F   385

20

21   1 @ Au + 1 @ C_4H_9- + 2 @ F   368

22

23   1 @ Au + 2 @ C_4H_9- + 1 @ C_3H_7-

24   + 2 @ F   269

25

26

27   UV analysis of an evaporated film of organoaurum

28   product supported on quartz shows that the material is

29   uv transparent in the range 900nm-350nm and hence the

30   material is suited for use in mask-making where uv

31   lithography is to be applied.

32

33   Studies have shown that the optimum solvent to be used,

34   both in the abstraction of the product material from

35   the phase separation stage of the preparation and in

1   the deposition of the material onto a quartz substrate,
2   is a low boiling point saturated alkane. Hence, the
3   product material was applied to the quartz substrate
4   using isopentane solvent.
5
6   The adhesion of organoaurum film to the quartz
7   substrate material is enhanced by exposing the coated
8   quartz substrate to microwave radiation prior to
9   electron beam bombardment. It is thought that this
10 process effectively evaporates off residual solvent –
11 trapped between the organoaurum film and the quartz
12 substrate to give better contact at the interface. The
13 quartz substrate can also be coated with the
14 organoaurum material via organometallic vapour
15 deposition technique (OMVD). The OMVD deposition
16 method results in a smoother more uniform coverage of
17 the organoaurum material compared to the solvent
18 application method.
19
20 Electron beam bombardment of the coated quartz
21 substrate was performed using a JEOL JSM-T220 Scanning
22 Microscope. The microscope was set at an accelerating
23 voltage of 20kV, focusing and movement of the sample
24 under the electron beam being both performed manually.
25 The organoaurum material easily reduced to the metal
26 component under the electron beam irradiation (Figure
27 8). The best line width attained to date using the
28 focussing power available on the JEOL instrument is
29 500nm.
30
31 A sample of the dibutylaurum (III) bromide dimer was
32 applied to the quartz substrate material and subjected
33 to electron beam bombardment. A film of reduced gold
34 metal was obtained on the quartz substrate.
35

1   Modifications and improvements can be made without

2   departing from the scope of the invention, for example

3   by using vapour phase deposition of the metal-

4   containing polymer.

5

6

7   Example 3

8

9   Preparation of Dibutylplatinum (IV) Fluoride dimer.

10

11   Magnesium turnings were degreased by washing in sodium

12   dried ether and transferred to a double-necked round

13   bottom flask containing a magnetic stirring bar.

14   Sodium dried ether was added sufficient to cover the

15   magnesium turnings. The flask was fitted with a water

16   cooled condenser and a dropping funnel charged with

17   5.62g dibutyl bromide (Aldrich Chemical Co.) in 80ml of

18   sodium dried ether. The butylbromide/ ether mixture

19   was added slowly and allowed to react with stirring

20   with the magnesium turnings. The system was left to

21   react for 2 hours at ambient temperature.

22

23   The prepared butylmagnesium bromide/ether mixture was

24   decanted to a dry dropping vessel and fitted to a

25   double necked round bottom flask containing 500mg of

26   platinum (IV) chloride (Aldrich Chemical Co) cooled

27   with powdered ice. The butylmagnesium bromide mixture

28   was added slowly with stirring to the platinum (IV)

29   chloride solution. After reaction powdered ice was

30   added to the reactant mixture and allowed to warm up to

31   ambient temperature.

32

33   The dibutylplatinum bromide dimer was extracted from

34   the reactant mixture using n-pentane in a phase

35   separation process. A dry methanol/ n-pentane phase

1   separation process was performed a further three times.
2   The product mixture was reacted with sodium fluoride in
3   dry methanol as described for the polydibutyltin
4   difluoride process.
5
6   The dibutylplatinum (IV) fluoride dimer product was
7   applied to a clean quartz substrate from an n-pentane
8   solution and n-pentane was driven off in a microwave
9   cooker to bake the product onto the quartz. The
10 microwave process ensured that the n-pentane was driven
11 off from the quartz interface instead of from its own
12 surface. This gave very good deposition of the product
13 on the quartz and allowed very good definition after
14 electron beam bombardment. A film of reduced platinum
15 metal was obtained supported on the quartz substrate.
16
17 A sample of the dibutylplatinum (IV) bromide dimer was
18 applied to the quartz substrate material and subjected
19 to electron beam bombardment. A film of reduced
20 platinum metal was obtained on the quartz substrate.
21
22 Examples 4-7
23
24 Preparation of Propyl, Tertiary butyl,
25 cyclohexylmethyl, benzyl analogues
26
27 An analogous procedure to that described in Example 2
28 was performed to prepare the propyl, tertiary butyl,
29 cyclohexylmethyl and benzyl analogues of organo gold
30 halides. The preparation of the organo magnesium
31 halide intermediate involved reaction of degreased
32 magnesium turnings with the ethernal solutions of the
33 appropriate propyl, tertiary butyl, cyclohexylmethyl
34 and benzyl bromides respectively.
35

1   Results:

2

3   a)   NMR analysis of the Propyl Auric Halide Material:

4

5   The ^{1}H NMR of the product material from the

6   reaction of the propyl magnesium Grinard with an

7   ethernal solution of auric (III) chloride is shown

8   in figure 9. The NMR shows peaks at 0.89 ppm

9   (triplet), and 1.29 ppm (multiplet) relative to

10   TMS (tetramethylsilane), which is consistent with

11   the spectrum expected from the propyl ligand. The

12   broad band at 1.57 ppm is consistent with that

13   expected for the -CH$_2$- adjacent to a group inducing

14   electron shielding. The ^{13}C NMR is shown in Figure

15   10. Although noisy, the spectrum shows three

16   peaks at 14 ppm, 22 ppm and 33 ppm relative to

17   TMS. The ^{13}C environments are consistent with CH$_3$-,

18   -CH$_2$- and a shielded -CH$_2$- respectively. The ^{19}F

19   NMR of the sample (proton coupled and decoupled)

20   showed a singlet at -67.64 ppm relative to CCl$_3$F

21   indicating that the material contained fluorine in

22   a symmetrical field.

23

24   The product material was applied to a quartz

25   substrate as described in Example 2. Electron

26   beam bombardment was applied to the coated quartz

27   material as described in Example 2. The material

28   reduced under the electron beam bombardment to

29   give gold lines identical to those obtained from

30   the tetrabutyl diaurum difluoride material.

31

32   b)   NMR analysis of the Benzyl Auric Halide Material:

33

34   The ^{1}H NMR spectrum of the product material is

35   presented in figure 11. The NMR data shows major

1   peaks at 7.3 ppm (multiplet) and 2.9 ppm (singlet)

2   relative to TMS. Smaller peaks consistent with

3   trace quantities of isopentane are also evident.

4   The spectrum shows that the product material

5   contains ligated benzyl groups. The ^{13}C spectrum

6   is presented in figure 12. The spectrum shows

7   peaks at 141.7 ppm, 128.5 ppm, 128.3 ppm, 125.9

8   ppm and 37.9 ppm relative to TMS. The ^{13}C

9   environments are consistent with the distribution

10 of shielding effect over the benzyl group ligated

11 to an electron inducing species. The ^{19}F NMR

12 showed a singlet at -67 ppm relative to CFC-11,

13 similar to those obtained for the previous

14 samples.

15

16 The product material from the benzyl Grinard

17 reagent reaction with an etheral solution of auric

18 (III) chloride was applied to a clean quartz

19 substrate and subjected to electron beam

20 bombardment as described in Example 2. The

21 material did not reduce to give metal lines.

22

23 c)   NMR analysis of the t-Butyl Auric Halide material.

24

25 The ^{1}H NMR analysis of the product material from

26 the reaction of the t-butyl Grinard reagent with

27 an etheral solution of auric (III) halide is

28 presented in figure 13. The NMR data shows the

29 presence of a major peak at 1.24 ppm (singlet)

30 relative to TMS which is consistent with that

31 expected for the t-butyl group. Impurities in the

32 NMR have been identified to be MeOH, TMS and $CHCl_3$.

33 Peaks consistent with some trace hydrocarbon

34 solvent are also observed. The ^{19}F NMR analysis

35 showed one peak at -67 ppm relative to CFC-11.

1 The product material from the reaction was applied
2 to a clean quartz substrate and subjected to
3 electron beam bombardment as described in Example
4 2. The material did not reduce to give gold metal
5 lines.

6

7 d) NMR analysis of the Cyclohexylmethyl Auric (III)
8   Material:

9

10 The ^{13}C NMR spectrum is presented in figure 14.
11 The spectrum shows peaks at 36.15 ppm, 34.67 ppm,
12 33.6 ppm and a doublet at 26.6 ppm relative to
13 TMS. The spectrum is consistent with that
14 expected for methyl cyclohexane. The ^{1}H NMR
15 analysis is presented in figure 15. The spectrum
16 shows peaks at 1.2 ppm, (singlet) 1.6 and 1.7 ppm
17 (singlets), 2.9 and 3.25 ppm (doublets). The
18 spectrum is consistent with that of
19 methylcyclohexane. The ^{19}F spectrum is shown in
20 figure 16. A singlet peak at -68 ppm relative to
21 CFC-11 is again observed.

22

23 The product material from the methylcyclohexyl
24 aurum reaction was applied to a clean quartz
25 substrate and subjected to electron beam
26 bombardment as described in Example 2. The
27 material did reduce under the conditions used to
28 deposit fine lines of gold as observed under
29 optical magnification. The width of the gold
30 lines obtained were ca 500nm.

31

32

33 Example 8

34

35 Preparation of organoplatinum halide complex:

1   The preparation of platinum analogue materials was
2   performed analogously to those described in Example 2.
3   Propyl, butyl and methylcyclohexane analogues were
4   prepared. The respective organomagnesium halide
5   intermediate material was reacted with an etheral
6   solution of platinum (IV) chloride (Johnson Matthey) at
7   0°C. Phase separation of the product material was
8   performed as described in Example 2. The product
9   material obtained had a white waxy appearance similar
10   to that obtained from the gold complexes.

11

12

13   Results

14

15   a)   NMR analysis of the product material from t-Butyl
16   platinum fluoride:

17

18   The ^{1}H NMR analysis is presented in figure 17. The
19   NMR shows the major peak at 1.25 ppm (singlet)
20   with evidence of MeOH solvent in the sample. The
21   ^{19}F NMR analysis gave one peak at -67.66 ppm.

22

23   b)   NMR analysis of the Butyl platinic halide product.

24

25   The ^{1}H NMR of the product obtained from the
26   reaction of the n-butyl Grinard reagent with an
27   etheral solution of platinum (II) chloride is
28   presented in figure 18. The NMR shows peaks at
29   0.82 ppm (doublet), 1.28 ppm (singlet), 1.39 ppm
30   (singlet) and 1.5 ppm (singlet), relative to TMS.
31   The spectrum is consistent with that expected for
32   an n-butyl moiety. The ^{19}F NMR analysis of the
33   material showed a singlet peak at -67 ppm (Figure
34   19).

35

1   The product material was applied to a clean quartz

2   substrate and subjected to electron beam

3   bombardment as described in Example 2. The

4   material was readily reduced under the influence

5   of the electron beam to deposit a line of metallic

6   appearance.

7

8   c)   <u>NMR Analysis of the Propyl Platinic Fluoride</u>

9   <u>Material</u>:

10

11   The ^{1}H NMR spectrum was performed in deuterobenzene

12   solvent and is presented in figure 20. The

13   spectrum shows peaks at 1.33 ppm (singlet),

14   0.91ppm (singlet) and 0.39 ppm (singlet) relative

15   to TMS. The spectrum is consistent with that

16   expected for a propyl moiety. ^{19}F NMR analysis

17   gave a single peak at -67 ppm.

18

19   d)   <u>NMR Analysis of the Methylcyclohexyl Platinic</u>

20   <u>Fluoride Material</u>:

21

22   The ^{1}H NMR spectrum of the product material from

23   the reaction of the methylcyclohexyl Grinard

24   reagent with an etheral solution of platinum (II)

25   chloride is presented in figure 21. The spectrum

26   is consistent with that expected for the

27   methylcyclohexyl ligand. The ^{13}C carbon NMR is

28   also presented in figure 22. The spectrum also

29   confirms that the product material contains

30   ligated methylcyclohexyl groups.

31

32

33   <u>Example 9</u>

34

35   <u>Example of the Butylpalladium analogue complex</u>:

1   The preparation of the butyl palladium analogue was

2   performed as described in Example 2. The respective

3   organomagnesium halide intermediate material was

4   reacted with an etheral solution of palladium (II)

5   chloride. It was observed that the product material

6   was thermally unstable resulting in deposition of the

7   palladium component at around 50°C. The deposited

8   palladium metal had strongly adhered to the glass

9   surface and could only be removed using acids.

10

11   Results

12

13   The ^{1}H NMR analysis of the product material from the

14   butyl Grinard reagent with an etheral solution of

15   palladium (II) chloride is presented in figure 23. The

16   spectrum is consistent with that expected for a butyl

17   ligand a weak interaction with the ligated centre. The

18   ^{13}C NMR spectra shows the presence of 3 carbon

19   environments in the compound. The ^{19}F NMR again shows a

20   singlet peak at -67 ppm (Figure 25).

21

22

23   General Discussion

24

25   Examples 2 to 9 show that the butyl-, propyl- and

26   cyclohexyl- gold complexes are able to be reduced to

27   the metal component under electron beam bombardment.

28.   The preparation of the propyl- and cyclohexyl-

29   analogues of the gold complex show no rearrangement

30   during the synthesis treatment. The ^{1}H NMR spectra of

31   these compounds do not exhibit any splitting patterns

32   that are consistent with the incorporation of fluorine

33   into the organic ligand. Whether these compounds have

34   fluorine as a constituent in their structure remains to

35   be determined. The ^{19}F NMR signal for the product

- 24 .

1   materials indicate that fluorine is present in a form

2   which confers a symetrical field around the fluorine

3   environment. Given that fluorine has the ability to

4   affect neighbouring carbon atoms and cause coupling

5   over long ranges, it seems that whatever form the

6   fluorine is in, it is shielded from the organic ligands

7   so that coupling cannot take place.

8

9   The reaction of the n-butyl group to give sec-butyl

10 products gives rise to some questions about the

11 chemistry that is affecting the formation of the

12 butylauric (III) fluoride. Firstly, it is important to

13 note that the organic ligand itself does not contain

14 fluorine. No splitting of the proton signals are

15 observed in the proton spectra and there are no signals

16 in the ^{19}F NMR to indicate that hydrofluoroalkane groups

17 are present. Hence, the isomerisation step of the n-

18 alkane cannot be taking place during the fluorination

19 process. Isomerisation usually requires the production

20 of a carbocation species in the presence of F ions

21 during the reaction with the methanol solution of NaF

22 would immediately give rise to a fluorinated organic

23 ligand, for which there is no evidence. Hence, the

24 evidence suggests an intramolecular re-arrangement at

25 some stage in the production of the fluorided material.

26

27 The mass spectroscopic data gives a molecular ion of

28 661 amu, the fragmentation pattern of which is wholly

29 consistent with the formula (sec-butyl)$_4$ Au$_2$ F$_2$. It must

30 be remembered that the Au (III) is in a 5d^8

31 configuration that would give a square planar

32 arrangement, and would also consider the propensity of

33 gold to form bridging dimers. Thus, it is tentatively

34 submitted that the tetrakis sec-butyl aurum (III)

35 difluoride structure would be as follows:

25

```
 1
 2   H₃C
 3       CH₂                          CH₂      CH₃
 4          CH                    CH
 5   H₃C          F                        CH₃
 6          Au        Au
 7   H₃C          F                        CH₃
 8          CH                    CH
 9       CH₂                          CH₂
10   H₃C                                   CH₃
```

11
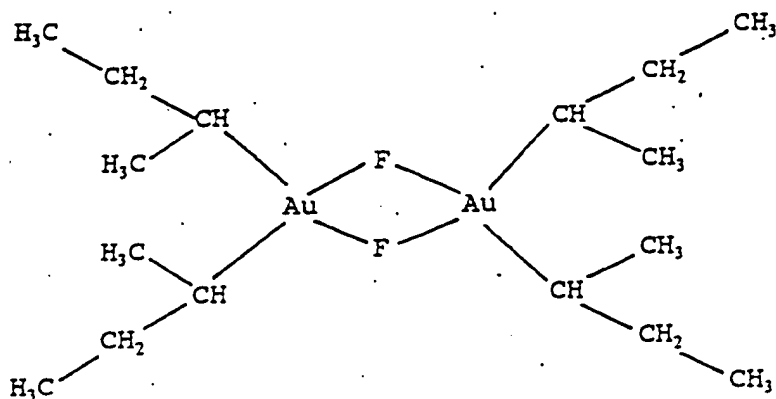
12 The organoaurum product is uv transparent in the region

13 from 900-3500nm. This is a positive result should mask-

14 making be an application for the material.

15

16 No deposition of metal lines was obtained from the

17 benzyl- and tertiary butyl- analogues. These materials

18 possess good inductive properties and are able to pump

19 electron density into neighbouring moieties. This may

20 have an effect on the reducibility of the gold

21 complexes.

22

23 Electron reduction has been successfully shown on the

24 butyl analogue of the Pt material. Also the cyclohexyl

25 analogue of the Pd materials were able to be reduced by

26 electron beam bombardment techniques. Thermal

27 degradation of the palladium complex at 50°C resulted in

28 a strongly bound metallic film of palladium that could

29 only be removed by reaction with acid. This result

30 indicates that the palladium analogue of the

31 organometallic complexes is a suitable candidate for

32 metal deposition by laser degradation.

1   CLAIMS

2

3

4   1.   A method of chemical deposition comprising

5   applying to a substrate a compound which degrades

6   under the effect of a radiant or particle beam to

7   produce a deposit and a degraded compound residue,

8   applying to selected areas of said compound a

9   radiant or particle beam and removing the degraded

10   compound residue and unaffected compound from said

11   substrate.

12

13   2.   A method as claimed in Claim 1 for manufacturing

14   an integrated circuit wherein said deposit is a

15   conductive material.

16

17   3.   A method as claimed in Claim 1 for manufacturing a

18   photomask wherein said substrate is a transparent

19   or translucent material and wherein said deposit

20   is opaque.

21

22   4.   A method as claimed in any one of Claims 1 to 3

23   wherein said compound is an organometallic

24   material.

25

26   5.   A method as claimed in any one of Claims 1 to 4

27   wherein said compound is an organometallic

28   fluoride.

29

30   6.   A method as claimed in any one of Claims 1 to 5

31   wherein said compound is an organometallic gold,

32   platinum, palladium or tin fluoride.

33

34   7.   A method as claimed in any one of Claims 1 to 6

35   wherein said compound is tetra-sec butyl diaurum

1   difluoride.

2

3   8.   A method as claimed in any one of Claims 1 to 7
4   wherein said compound is exposed to microwave
5   radiation after application to said substrate and
6   before application of said radiant or particle
7   beam.

8

9   9.   A method as claimed in any one of Claims 1 to 7
10   wherein said compound is applied to said substrate
11   by an organometallic vapour deposition (OMVD)
12   technique.

13

14   10.   A method as claimed in any one of Claims 1 to 9
15   wherein said compound is degraded by a laser beam,
16   an ultra-violet beam and/or an electron beam.

17

18   11.   An integrated circuit obtainable by the method as
19   claimed in any one of Claims 1, 2 and 4 to 10.

20

21   12.   A photomask obtainable by the method as claimed in
22   any one of Claims 1 and 3 to 10.

23

24   13.   An integrated circuit or photomask as claimed in
25   either of Claims 11 and 12 having nanoscale
26   resolution.

27

28   14.   An integrated circuit manufactured by use of a
29   photomask as claimed in either of Claims 12 and
30   13.

31

32   15.   A gold organometallic fluoride compound.

33

34   16.   Use of an organometallic compound in a method as
35   claimed in any one of Claims 1 to 10.

1   17. Use as claimed in Claim 16 wherein said
2   organometallic compound is an organometallic gold,
3   platinum, palladium or tin fluoride compound.
4
5   18. Use of a radiant or particle beam in the method as
6   claimed in any one of Claims 1 to 10.
7
8   19. A method of manufacturing an organometallic
9   fluoride compound suitable for use in the method
10   of Claims 5 to 10, wherein sodium fluoride is
11   added to said organometallic compound in its
12   chloride or bromide form.
13
14

1/28

FIG. 1
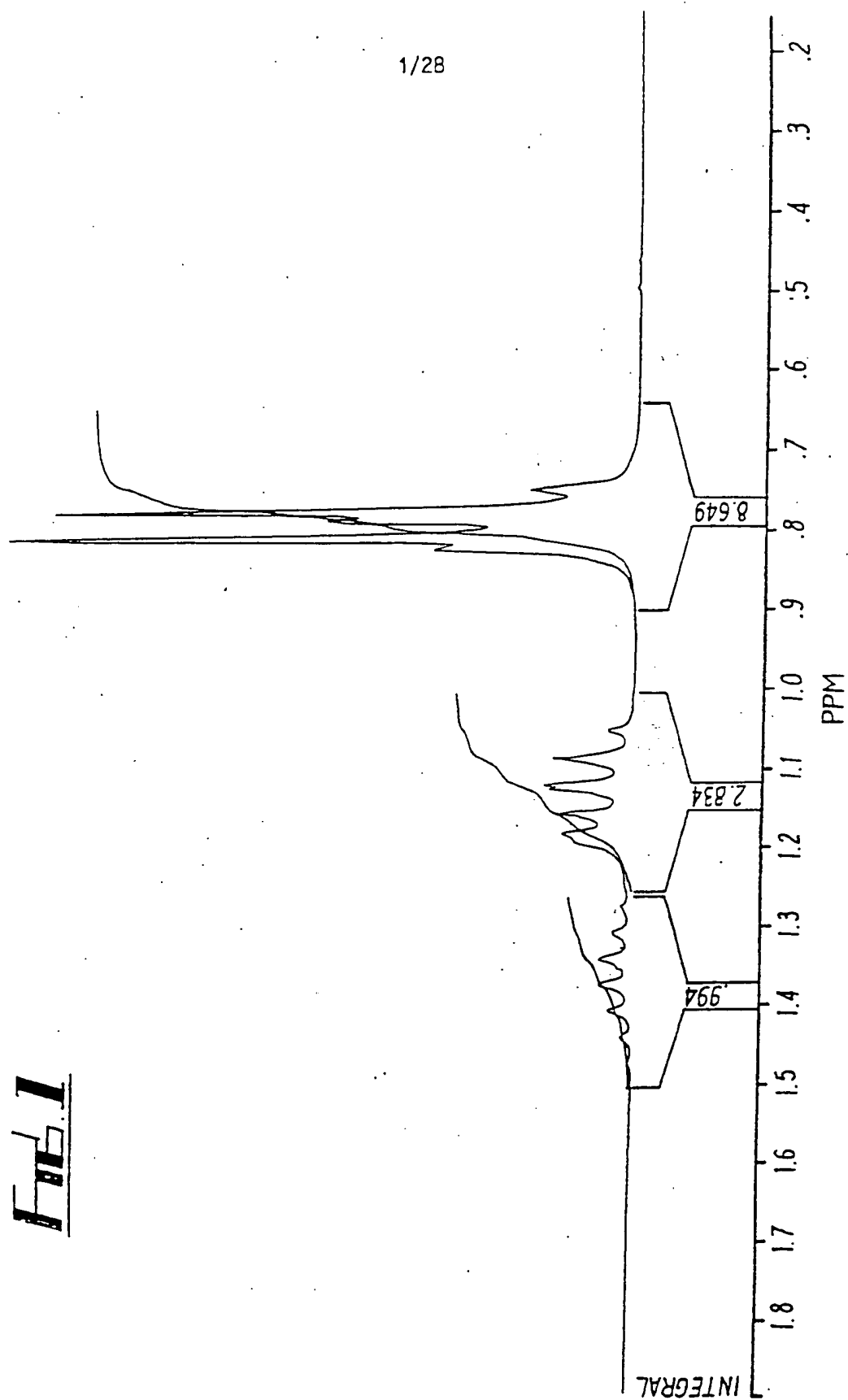
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225.074

165.437
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158.524
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151.512
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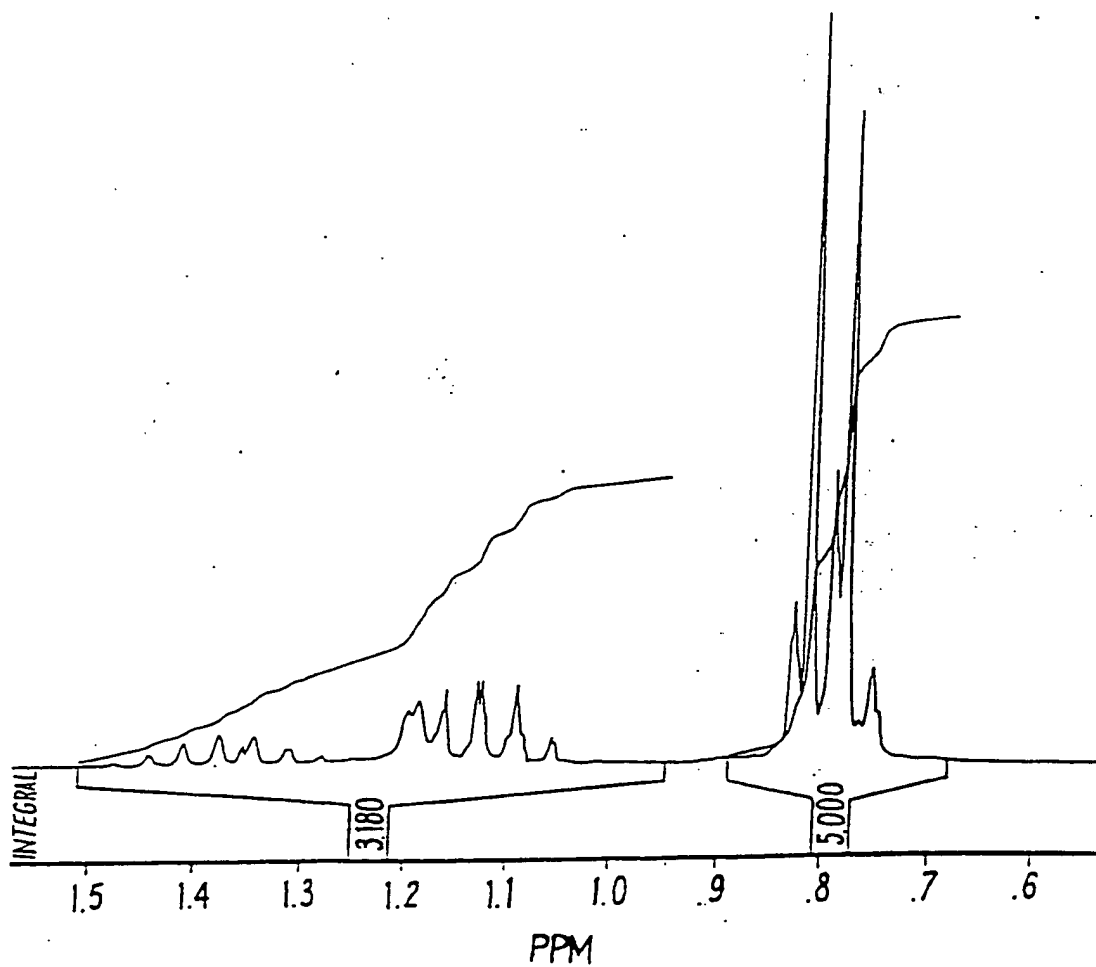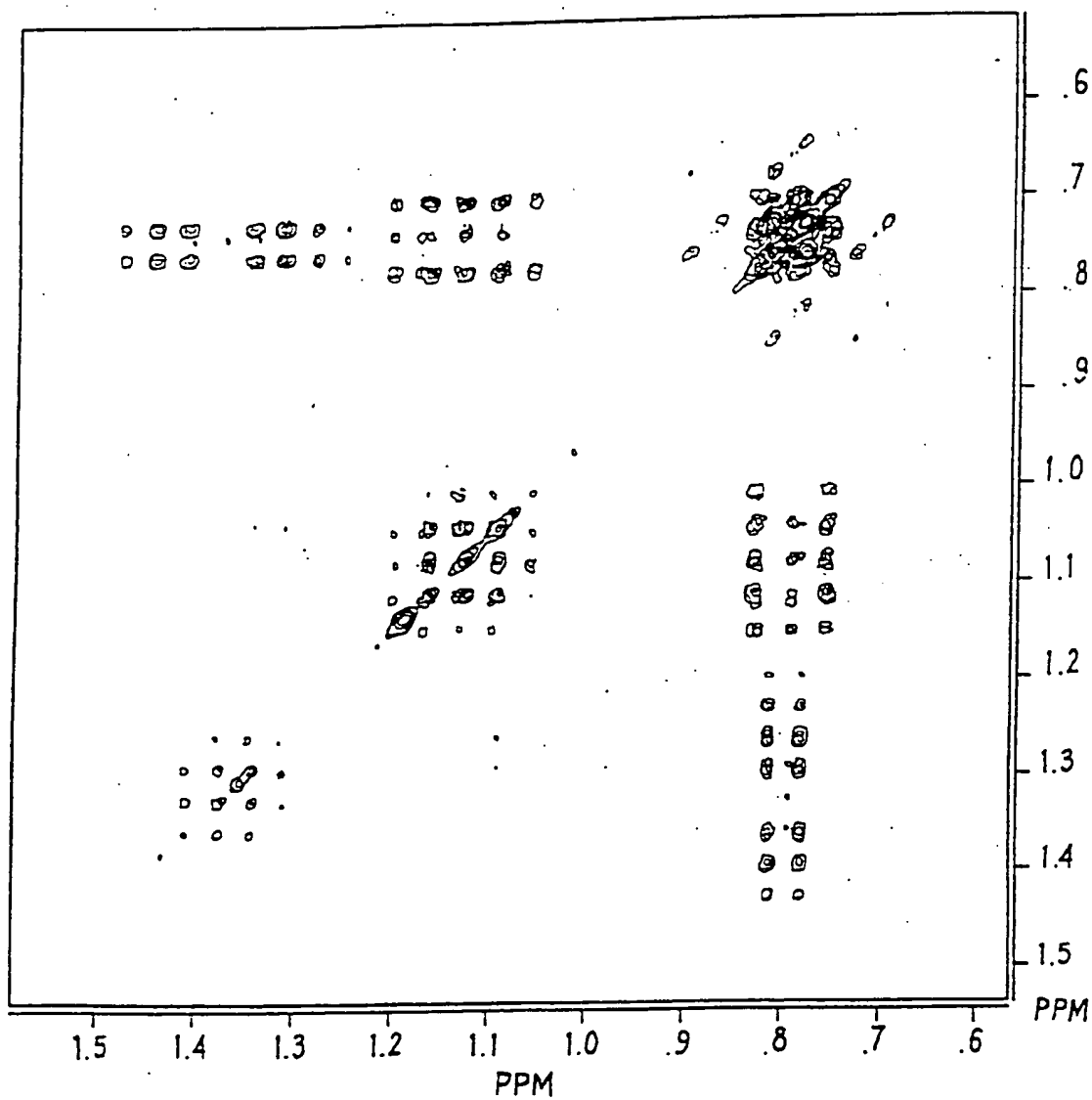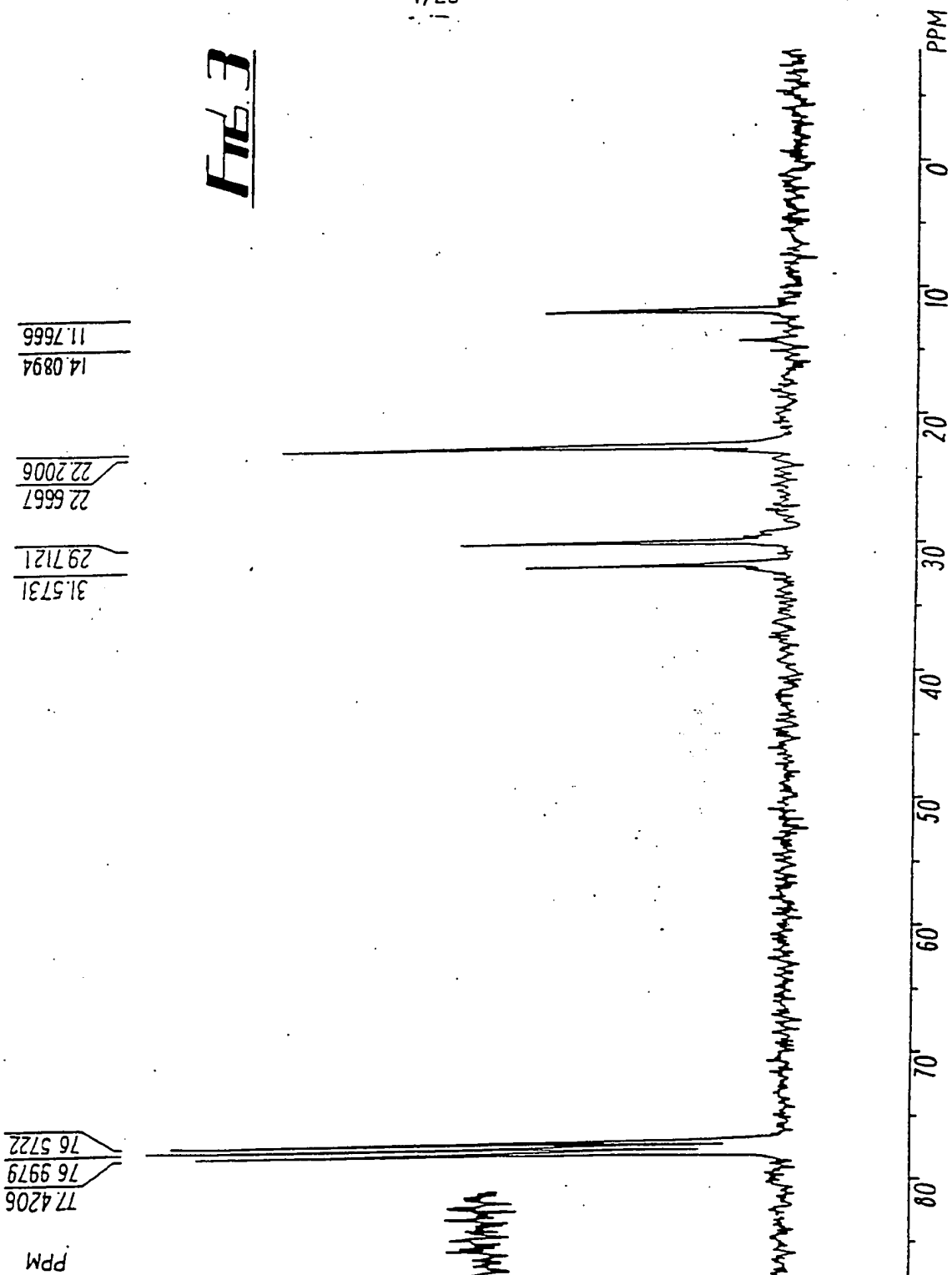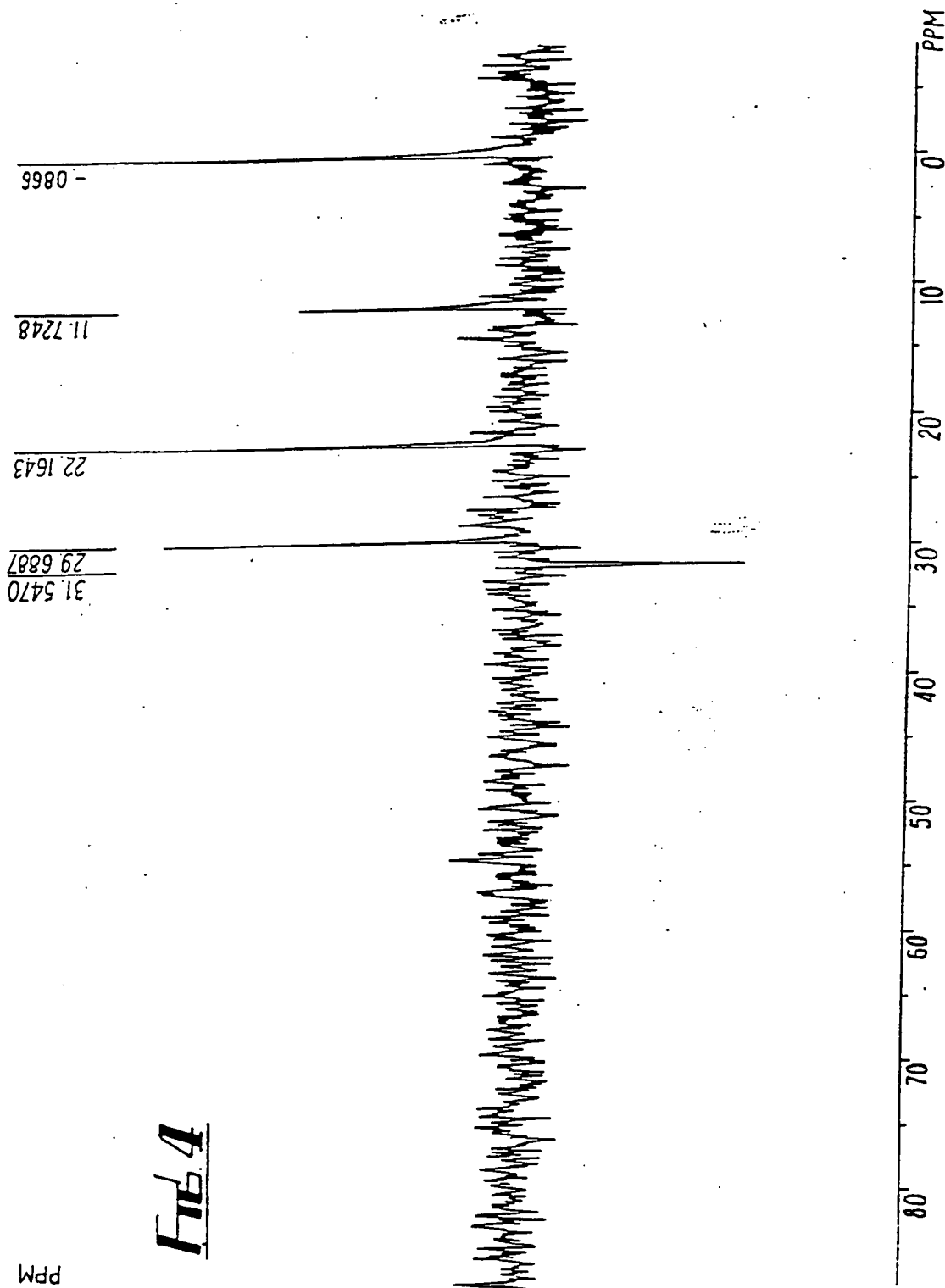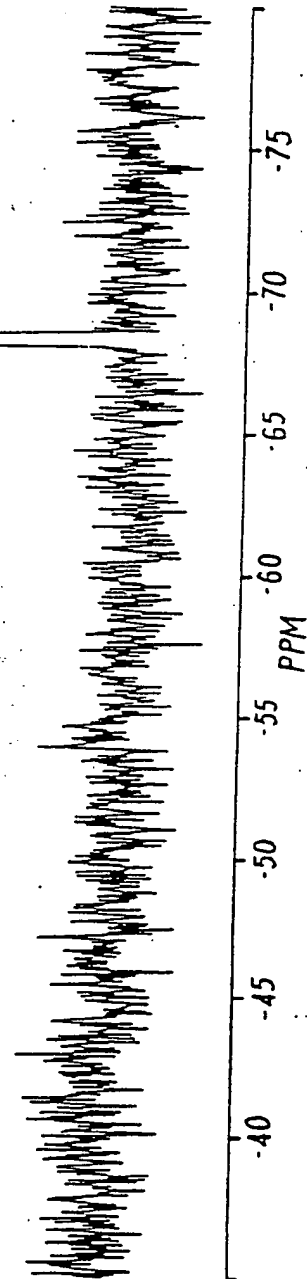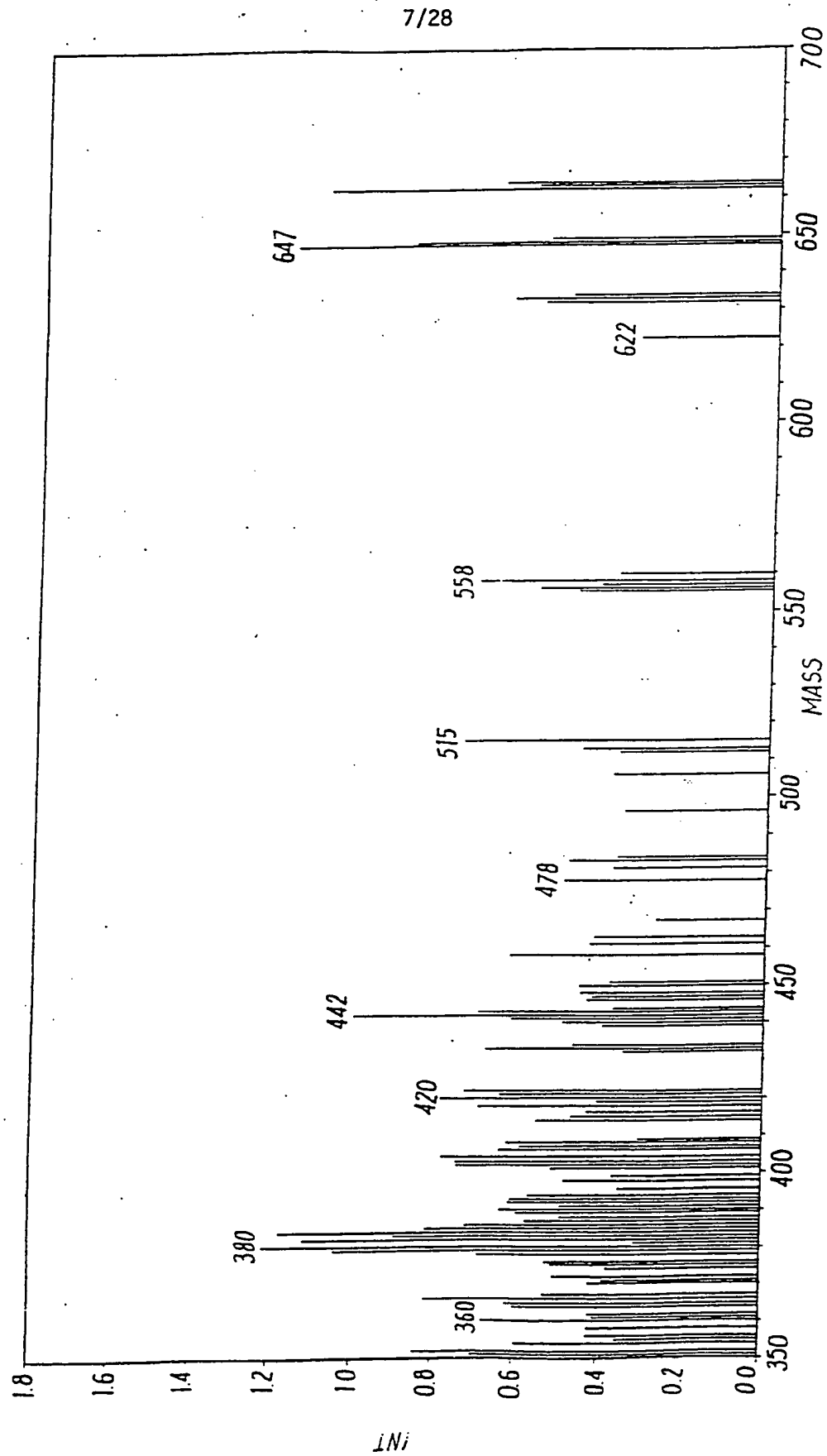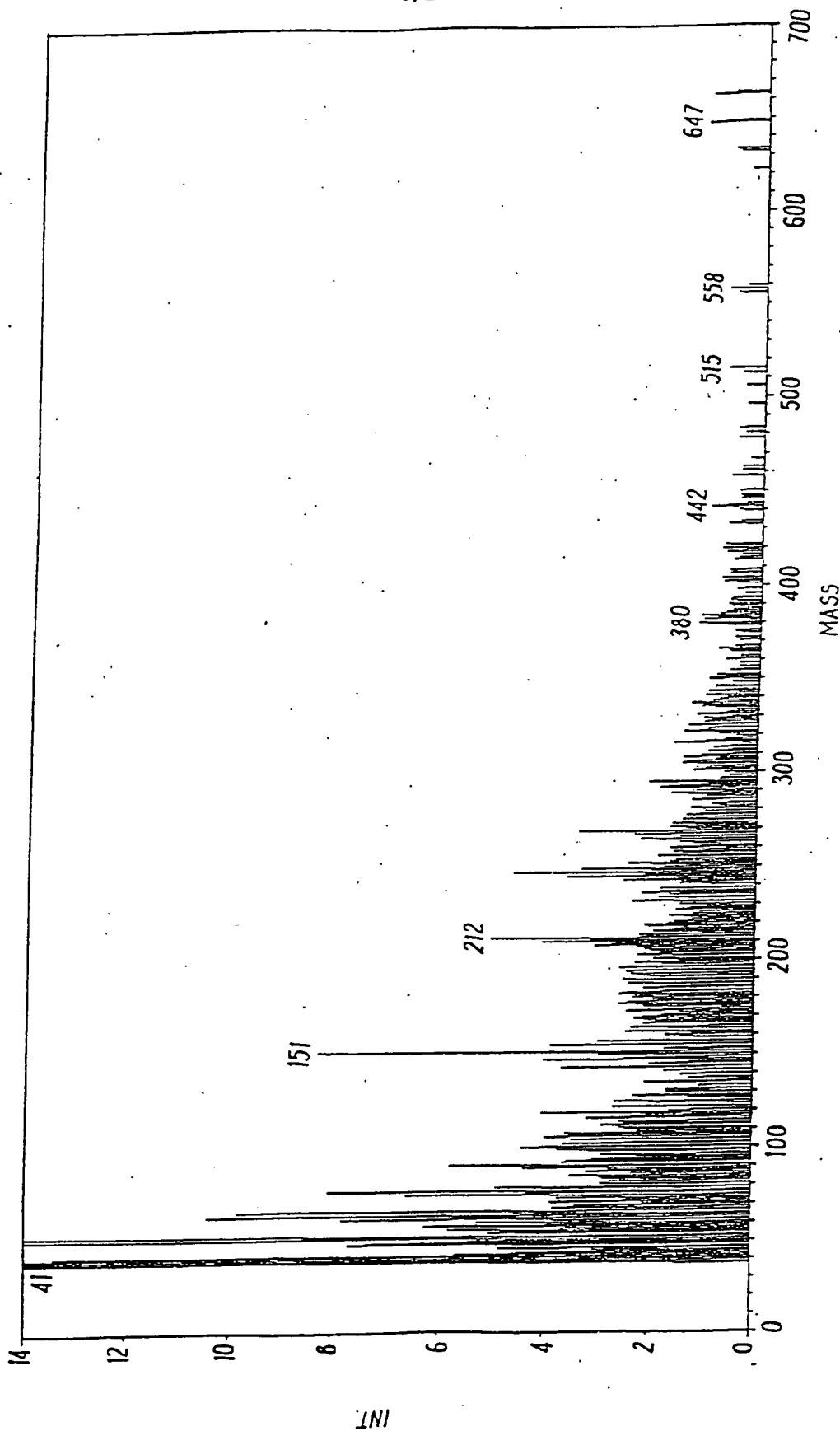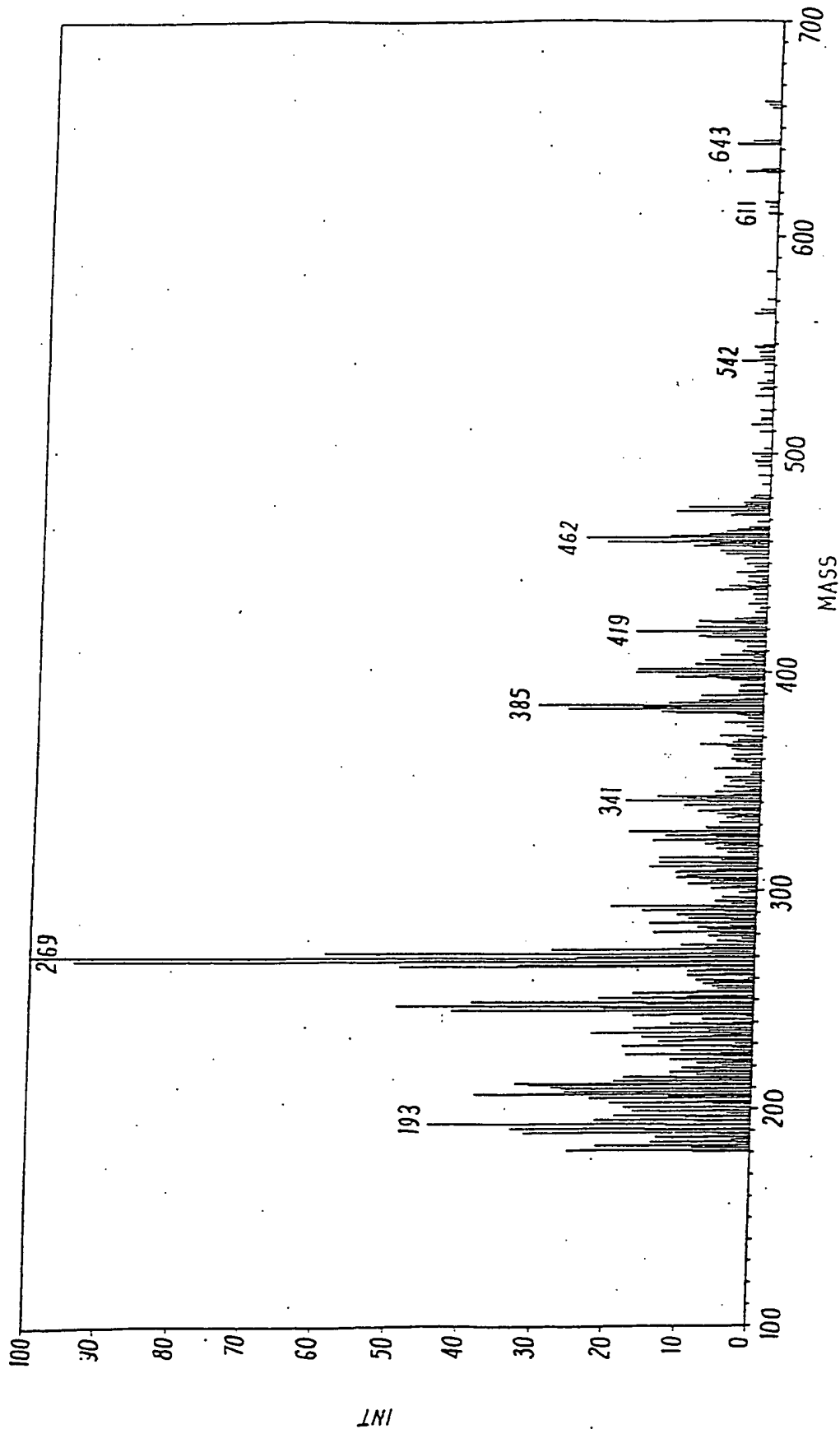
INTEGRAL

3180

5000

1.5   1.4   1.3   1.2   1.1   1.0   .9   .8   .7   .6

PPM

Fig. 1a

FIG. 2

Fig. 3

Fig 4

PPM

-0866

11.7248

22.1643

29.6887
31.5470

PPM

80   70   60   50   40   30   20   10   0   PPM

Fig. 5

Fig 6

Fig. 6a

FIG. 1

FIG. 1a

Fig 8

PPM

7.26089

1.57820
1.39200
1.37003
1.35788
1.32868
1.32160
1.29799
1.29354
1.26880
1.25650
1.25014
1.23055
1.21217
1.17708
0.96152
0.91417
0.89766
0.88288
0.84751
0.00000

Fig.9

9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0   0.0
PPM

PPM

77.6234
76.9908
76.3505

38.1446
31.9088
31.2216
29.6647
22.6789
14.1065

180   160   140   120   100   80   60   40   20   0
                          PPM

Fig. 10

FIG. 11

Fig. 12

FIG 13

Fig. 14

Fig. 15

FIG. 16

FIG. 17

Fig.18

Fig. 19

Fig. 20

FIG. 21

Fig. 22

Fig.23

14.087

22.628

34.386

127.398
127.679
128.360

PPM

Fig.24
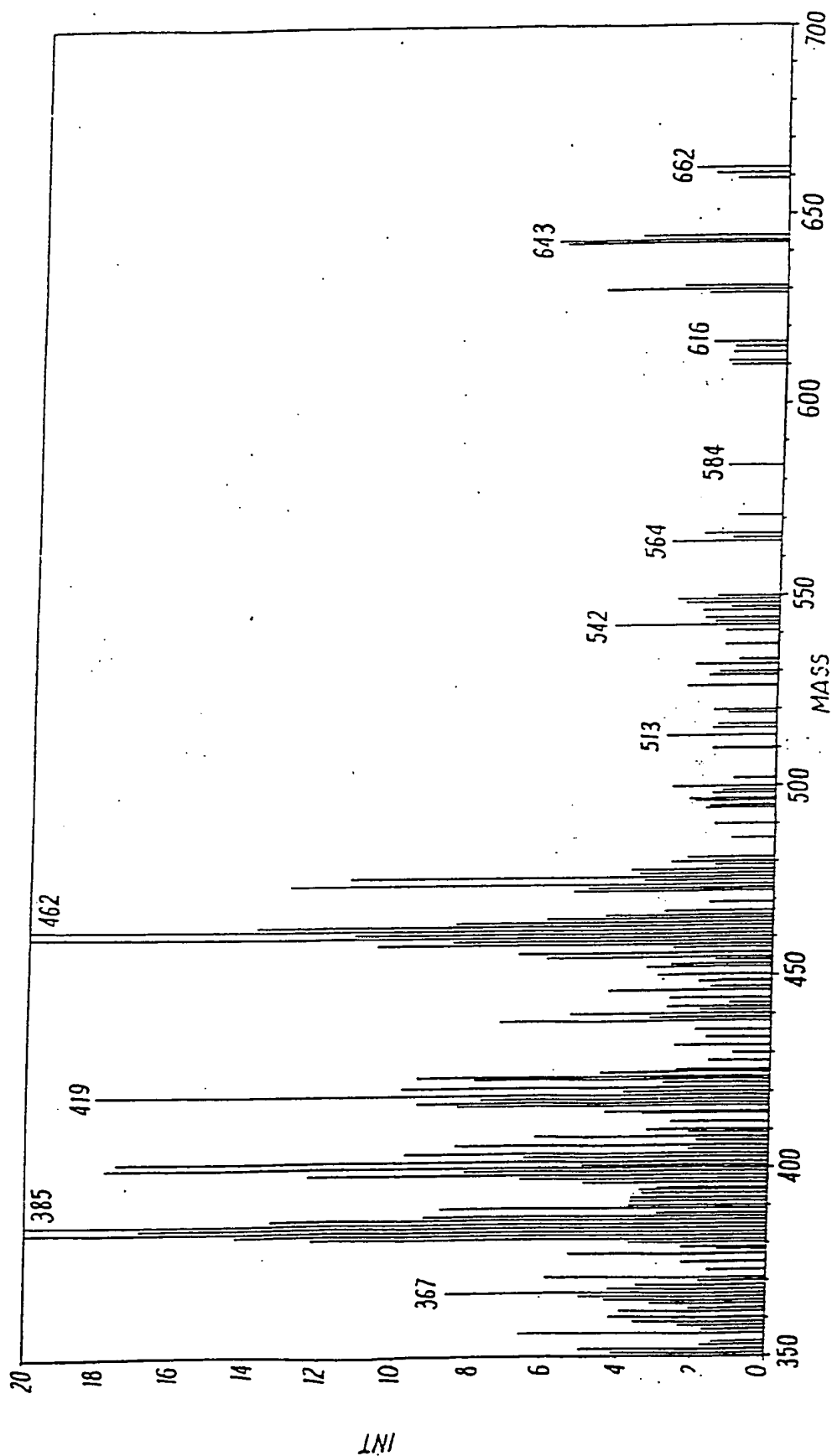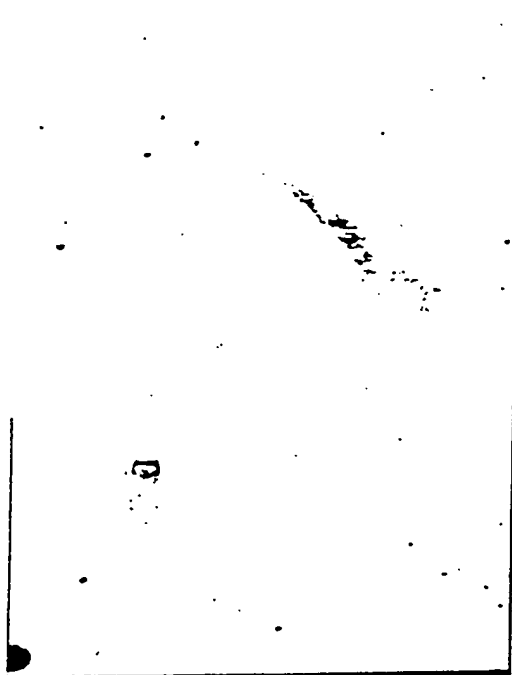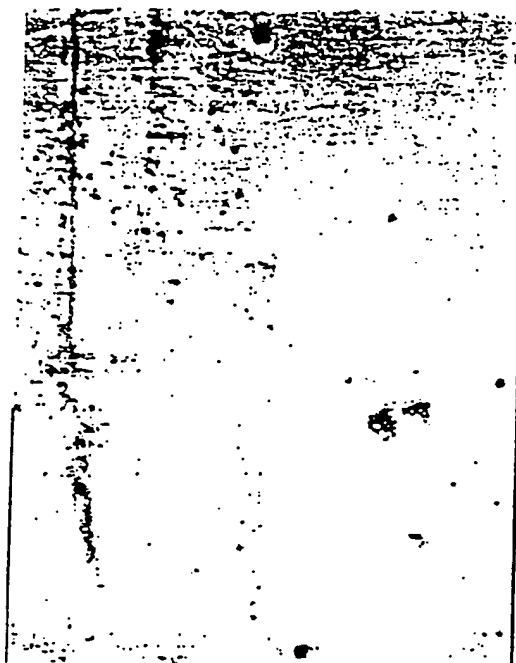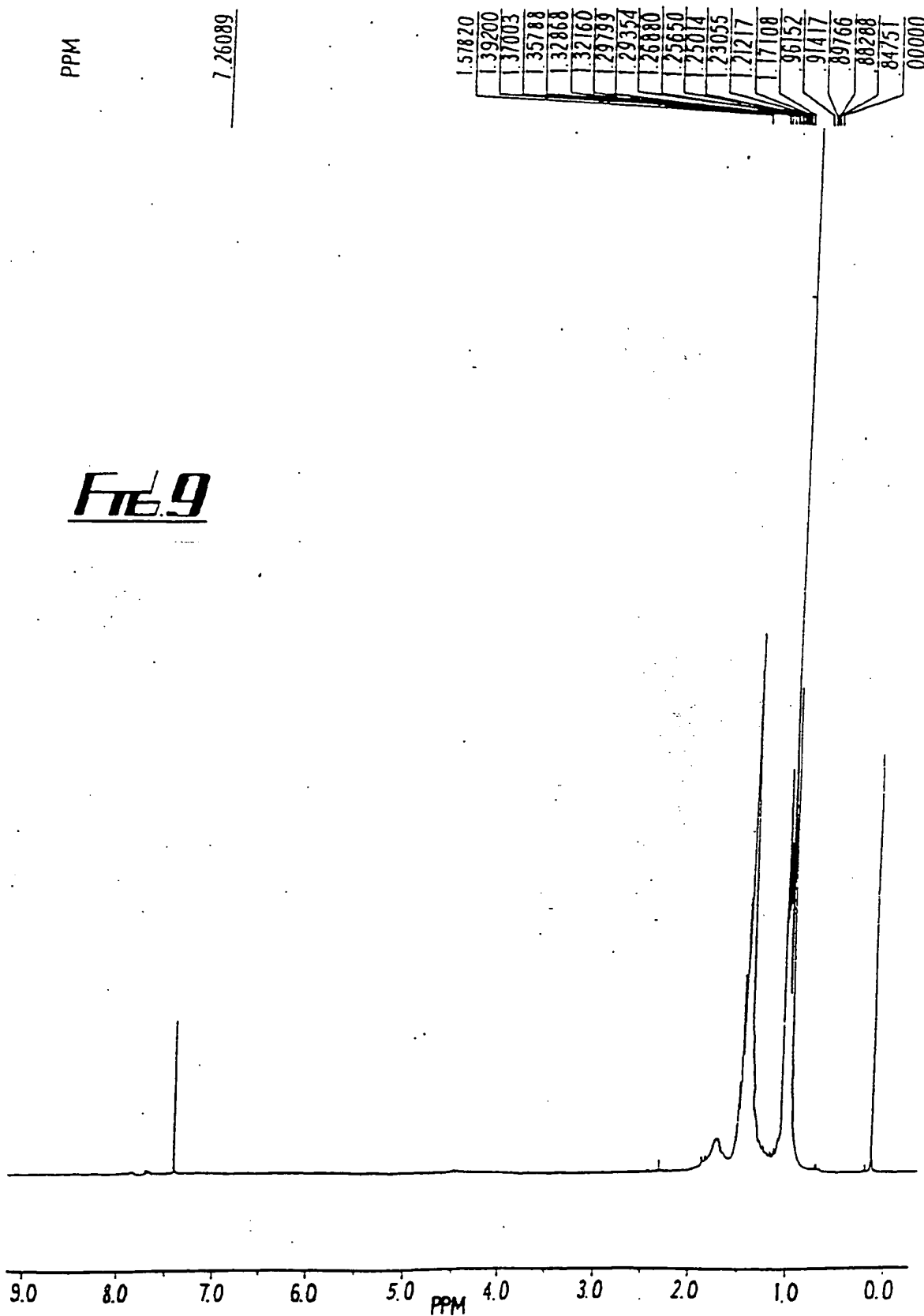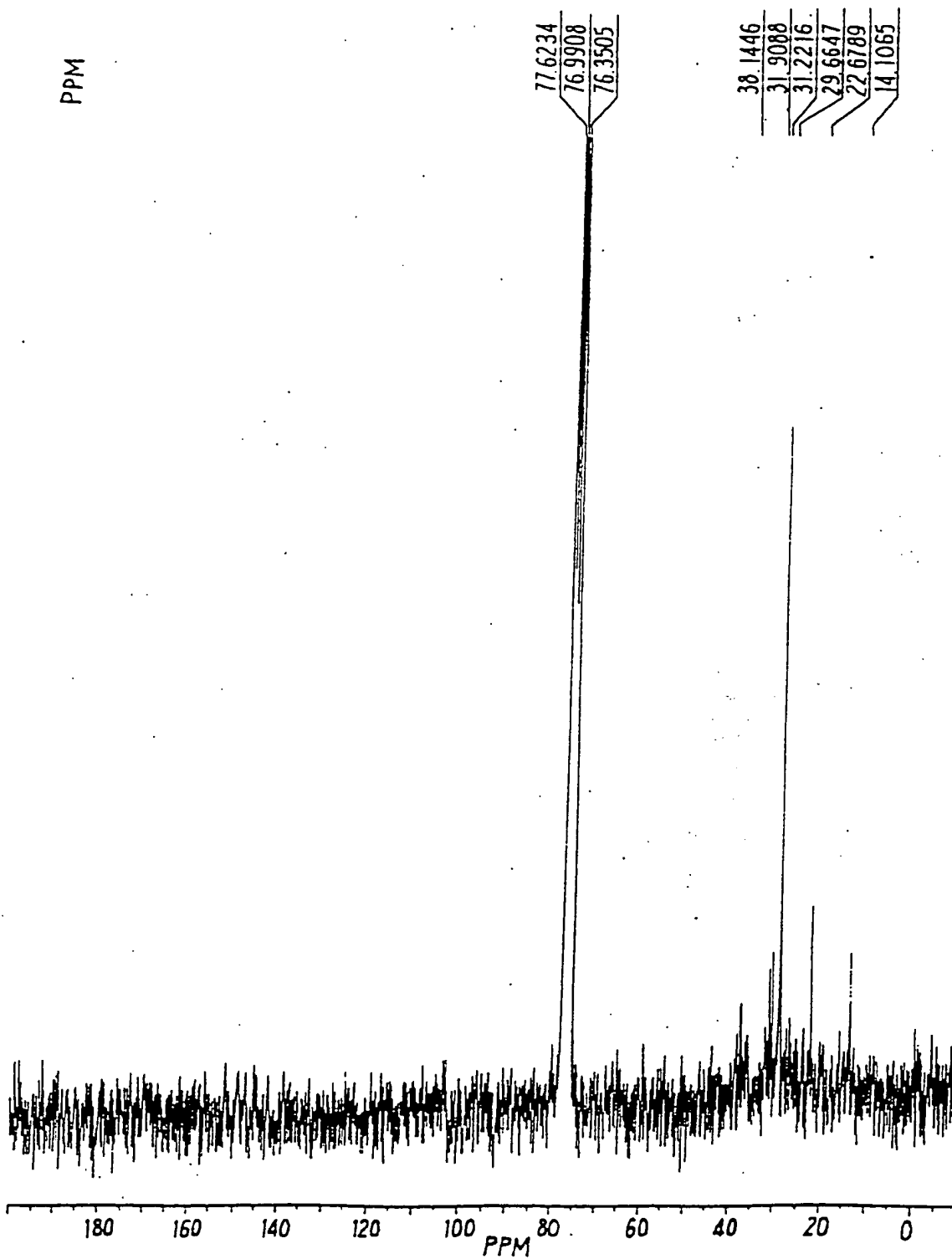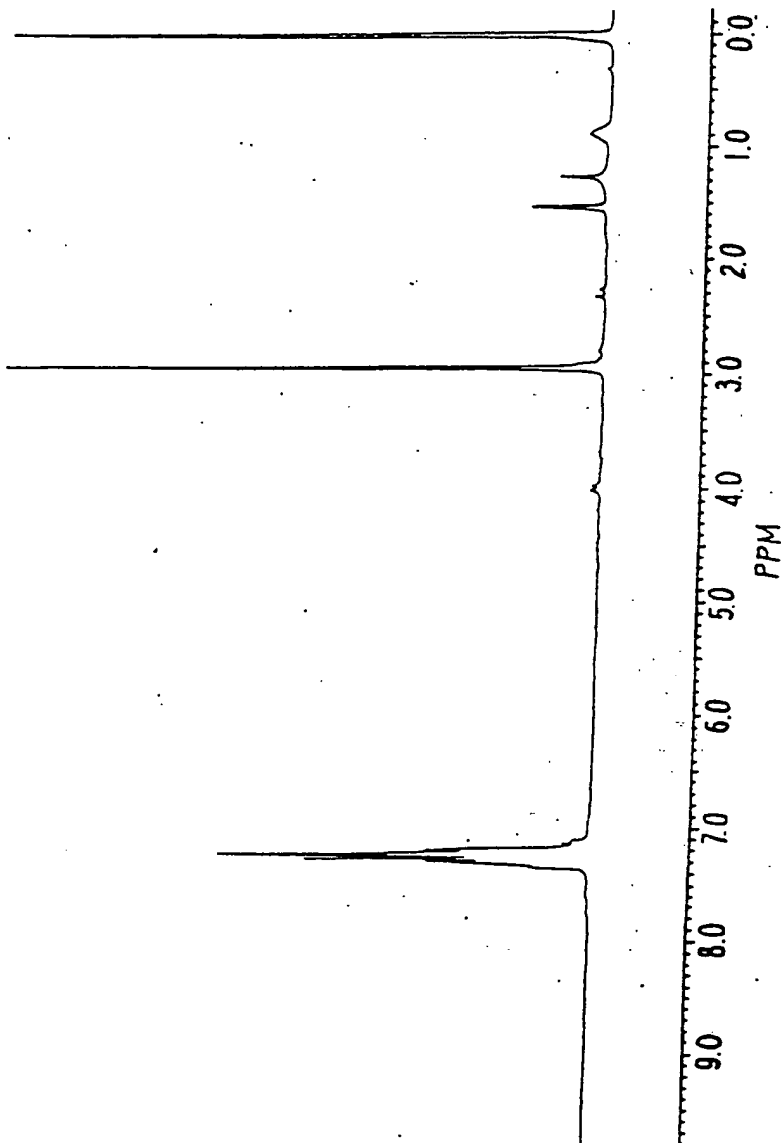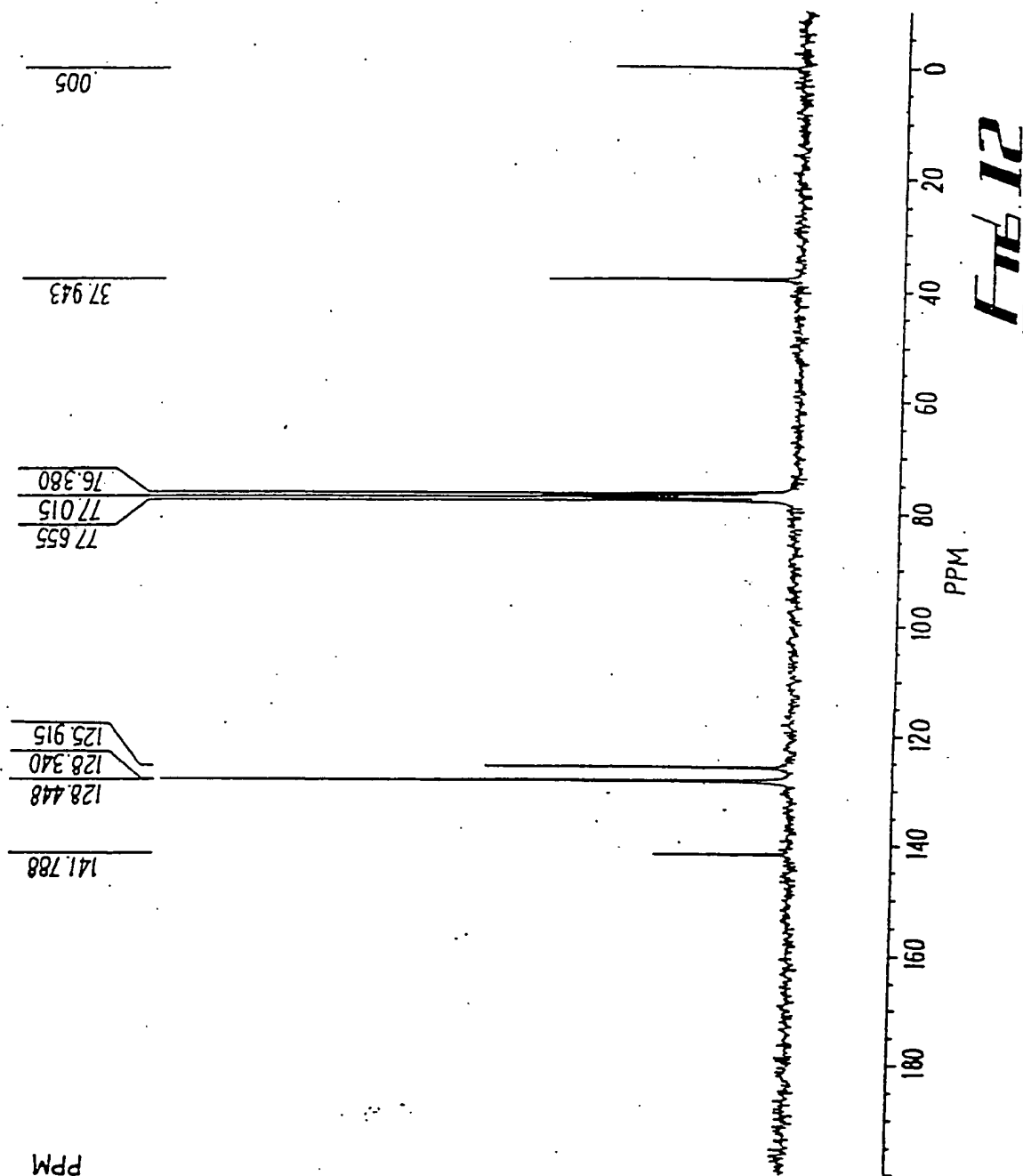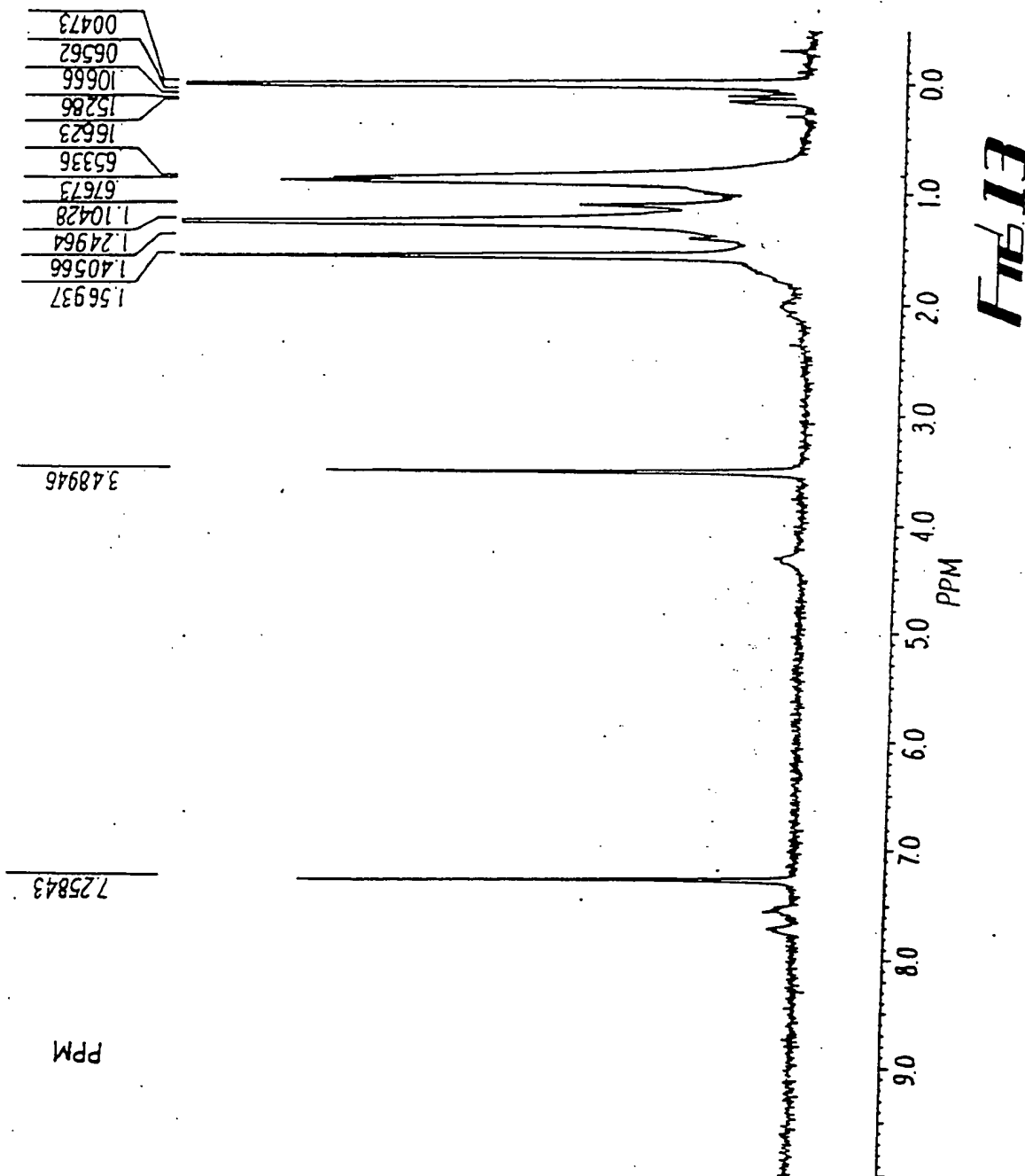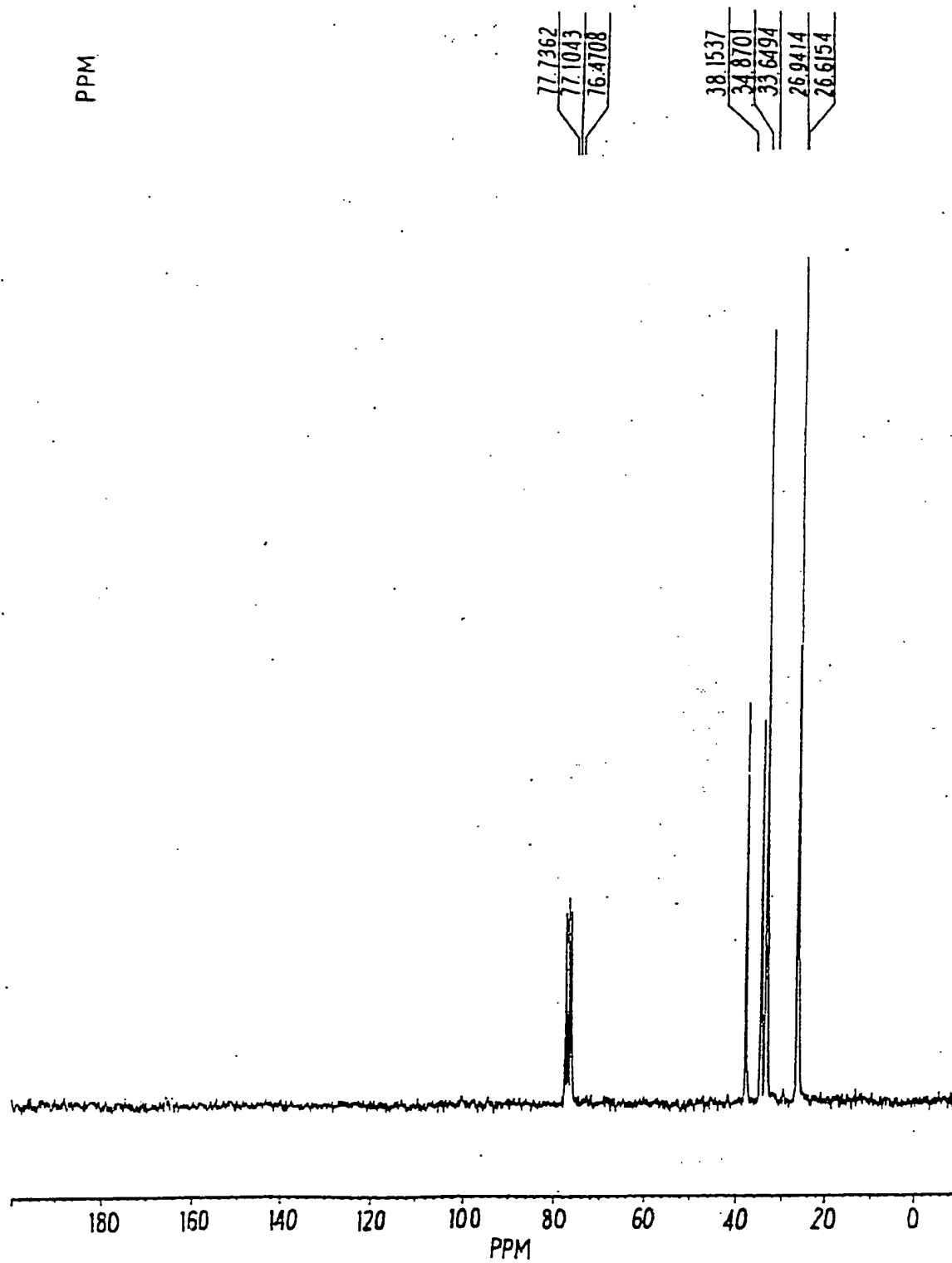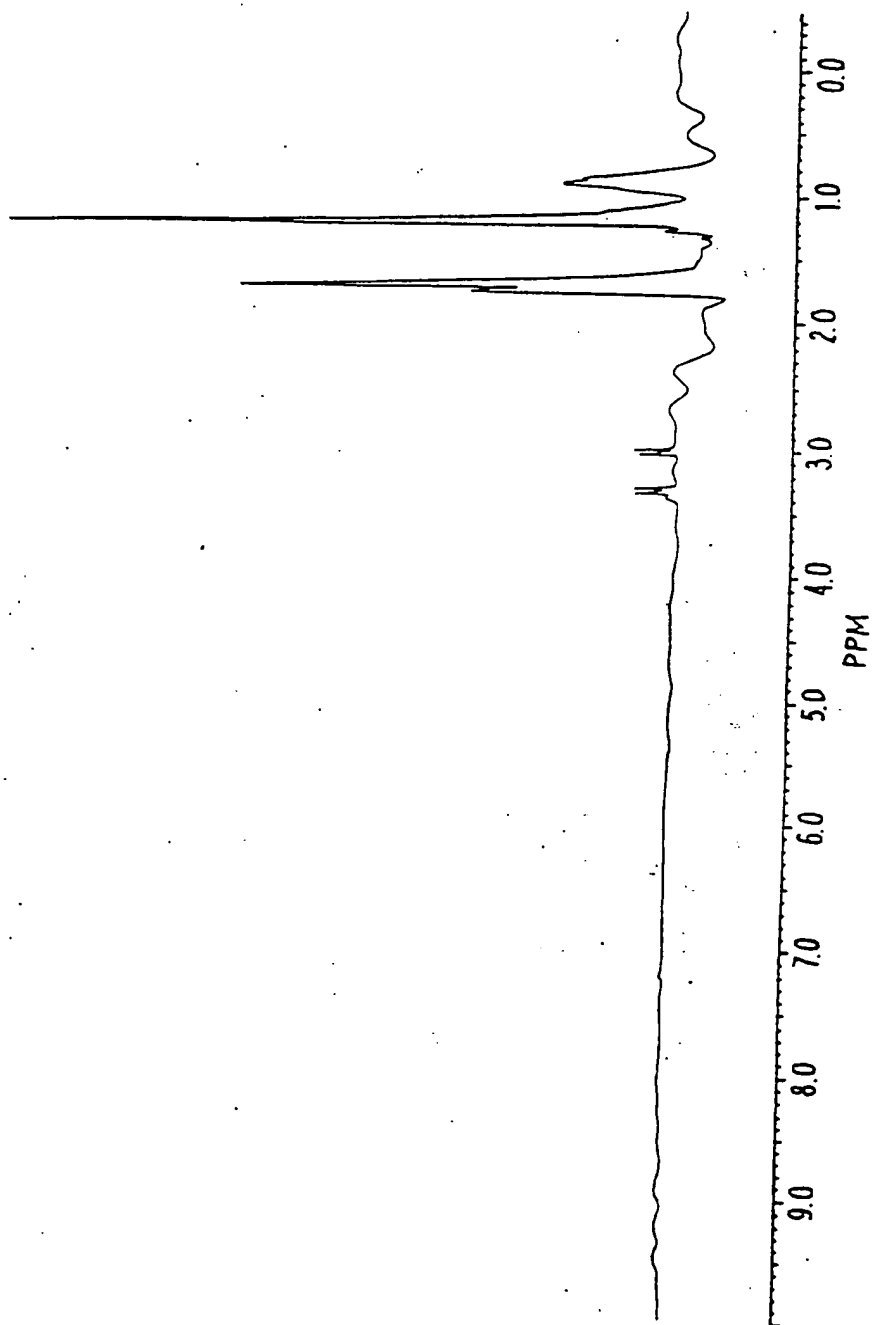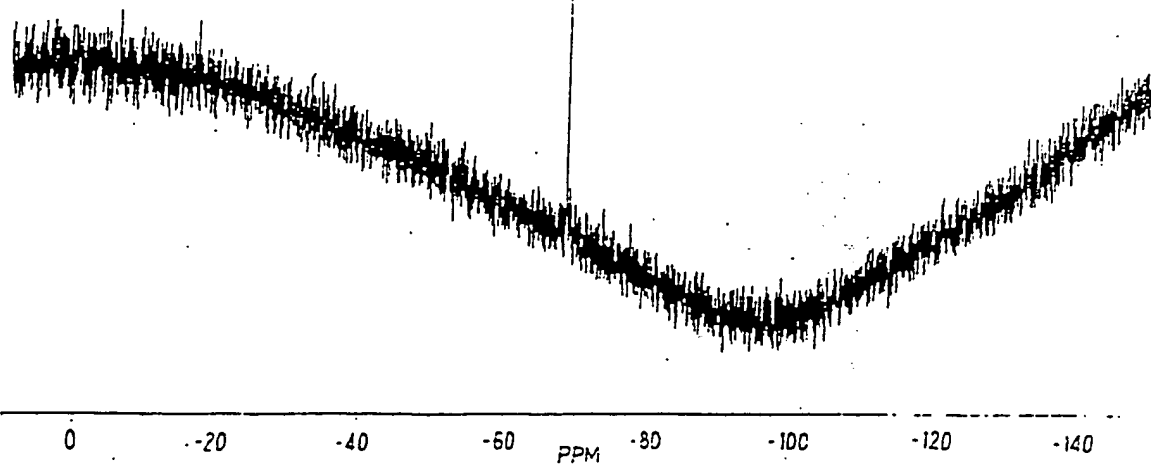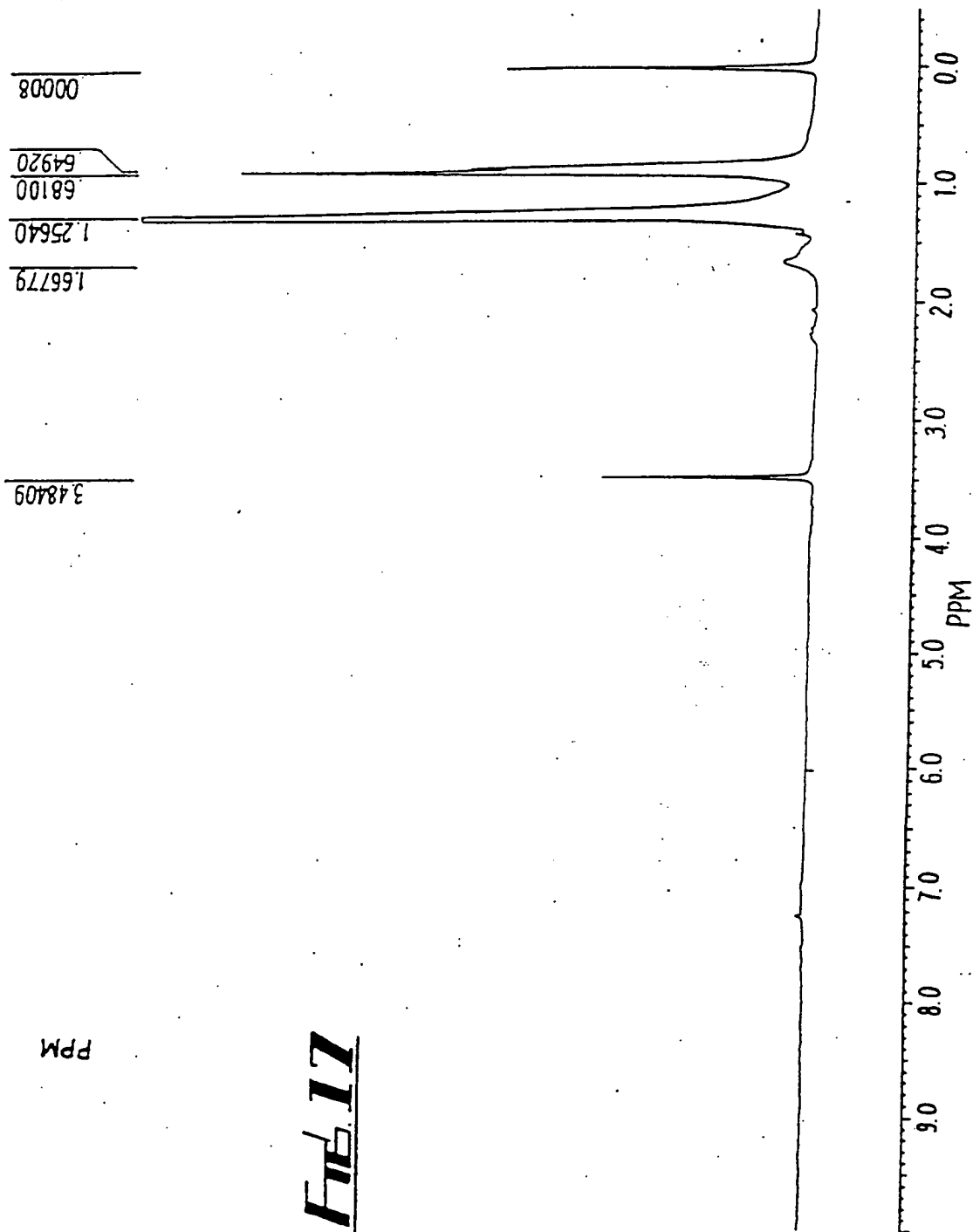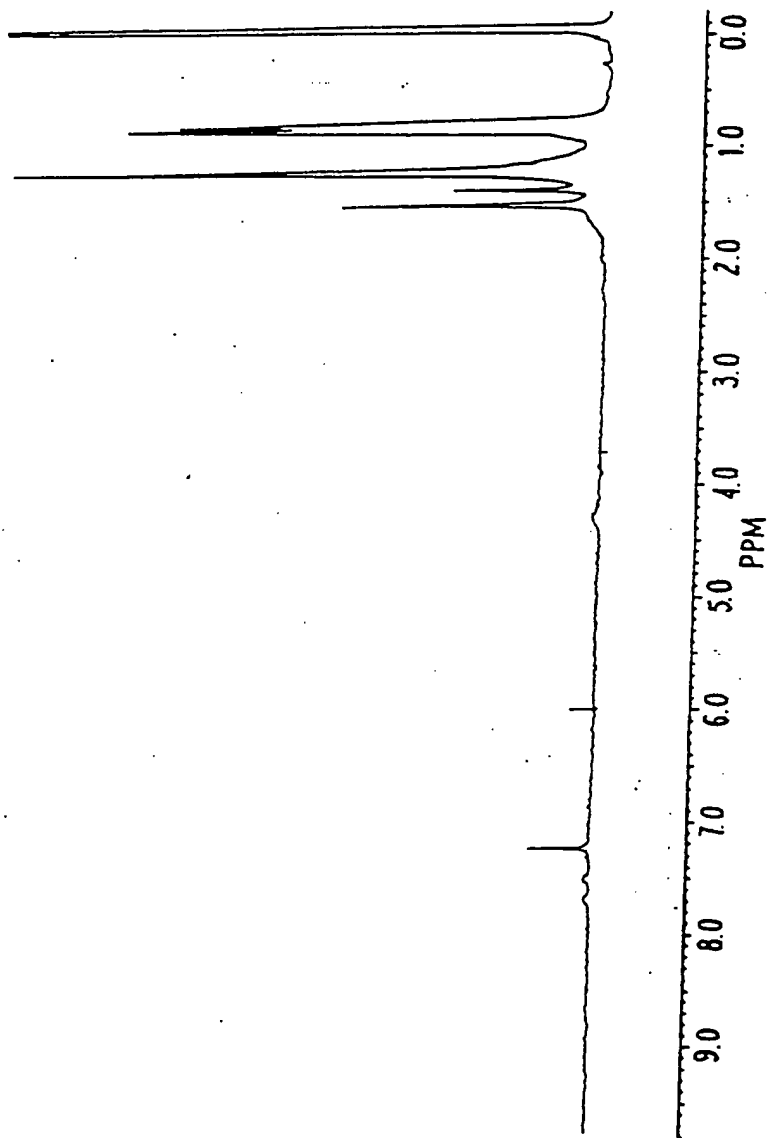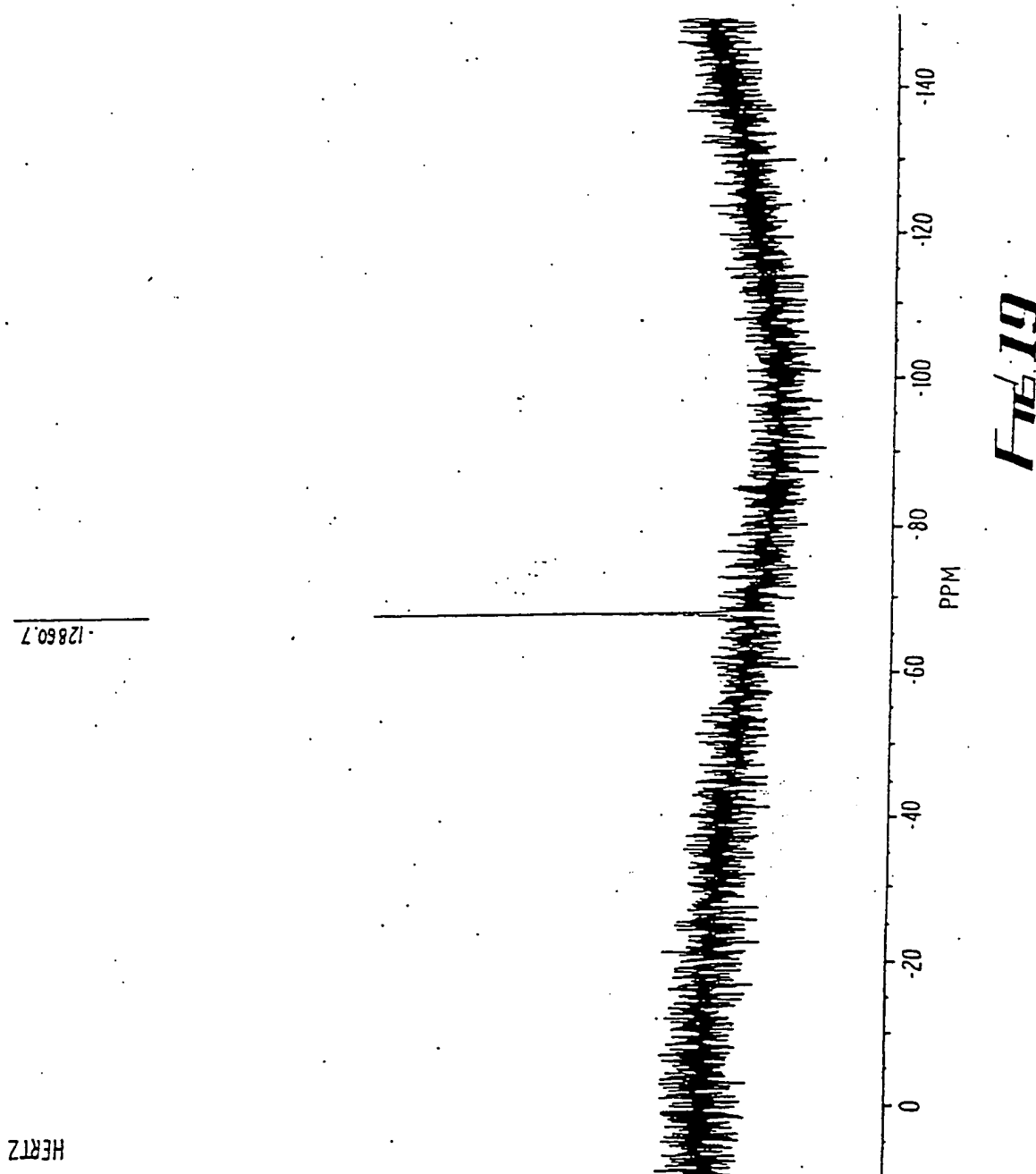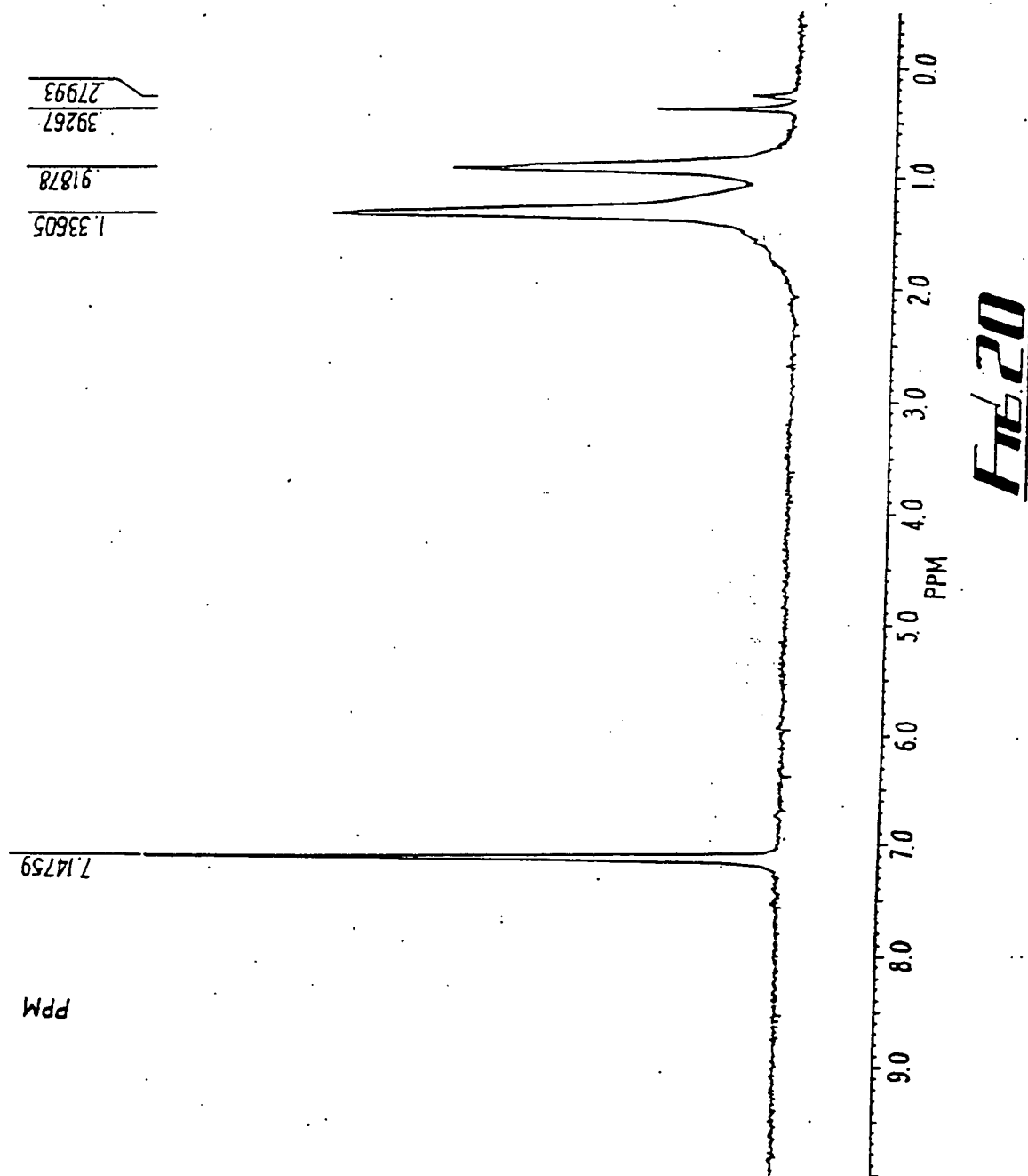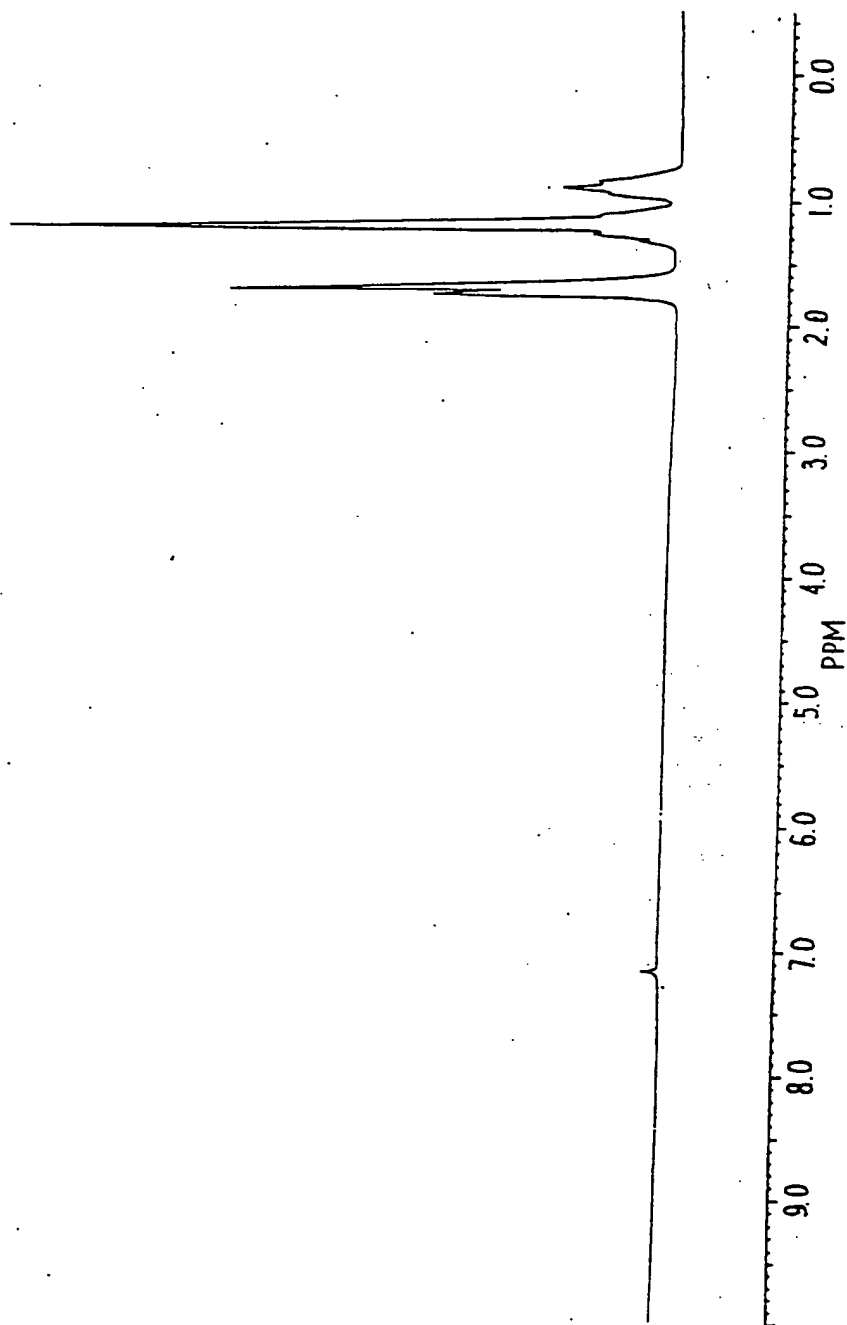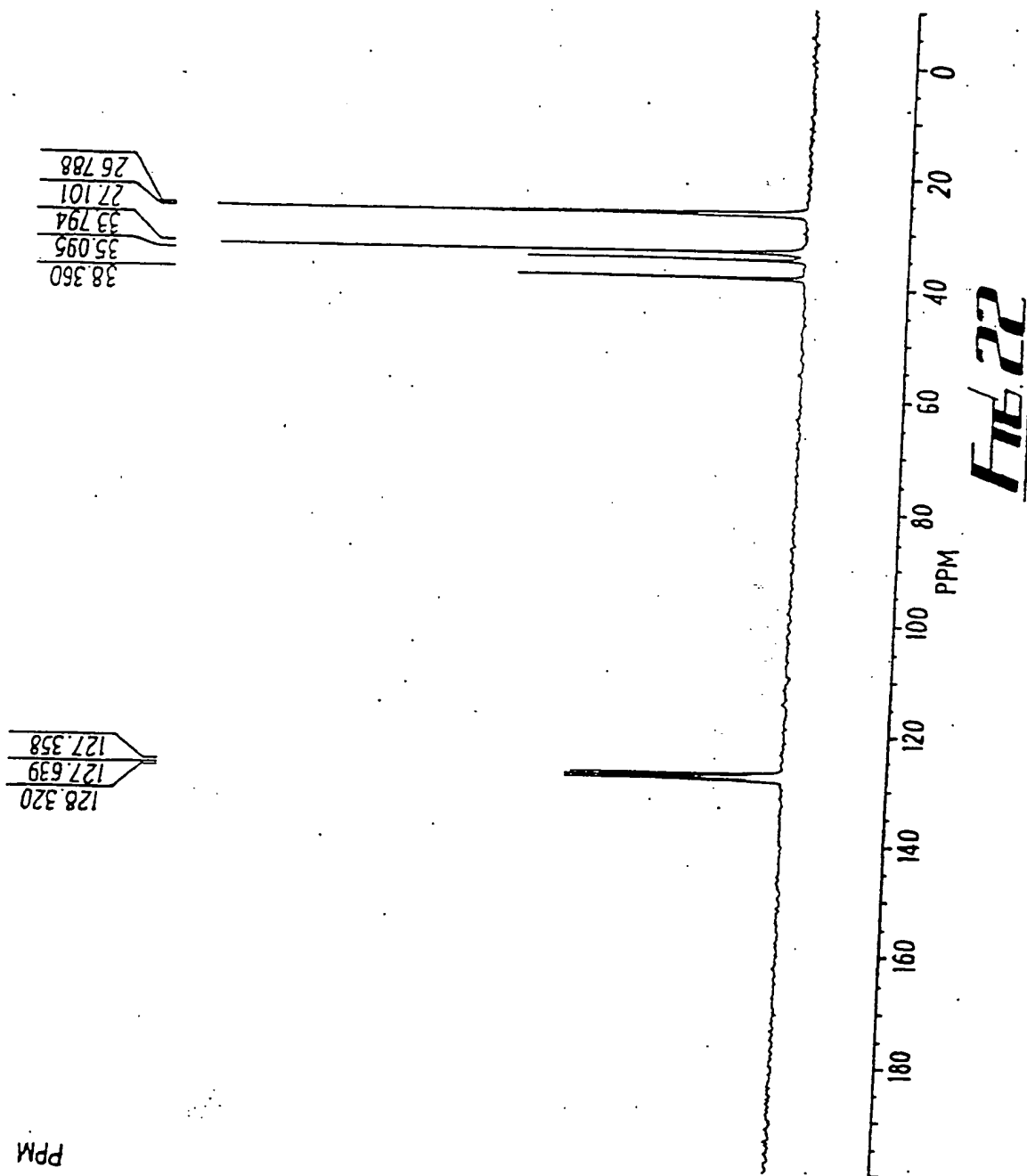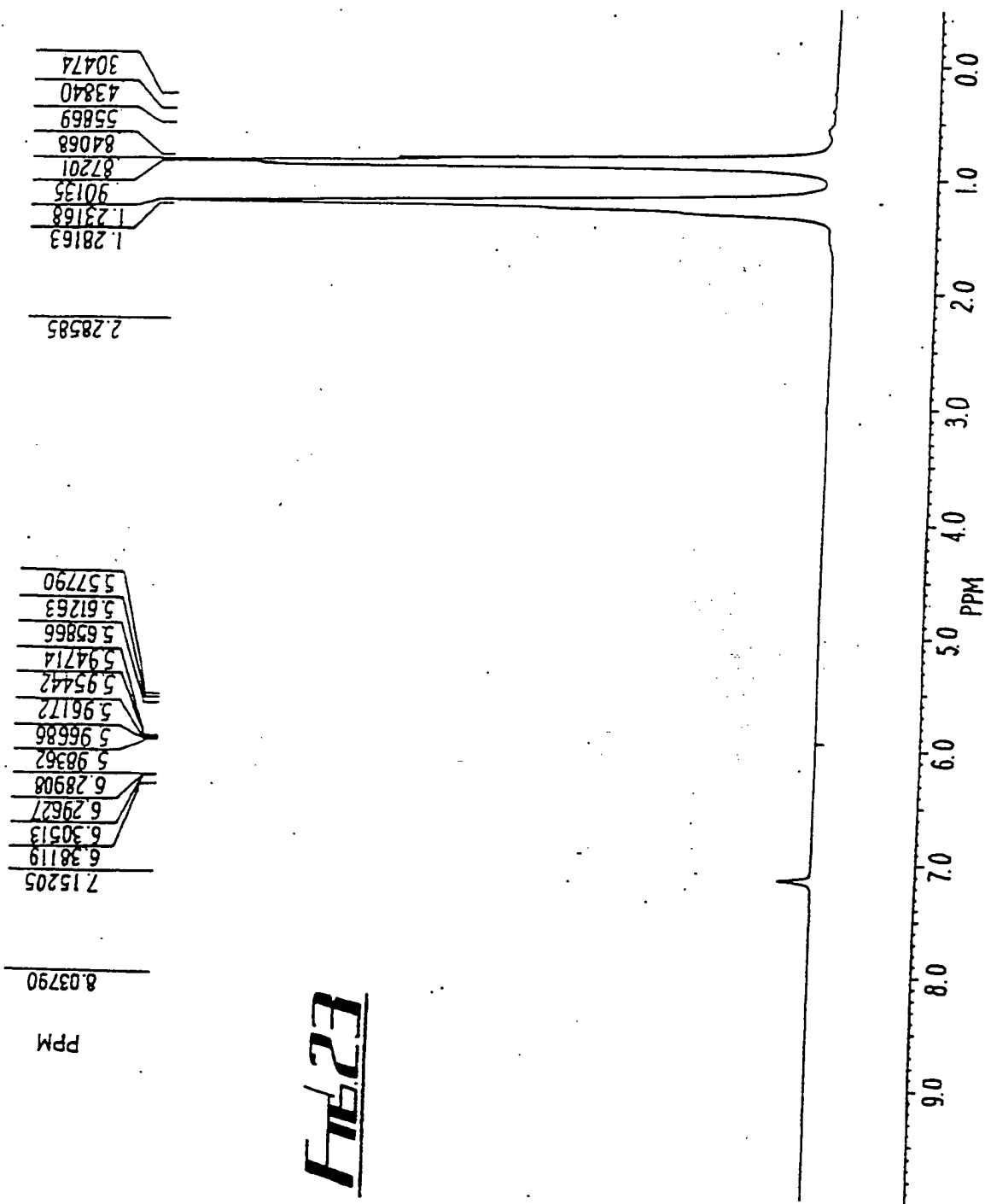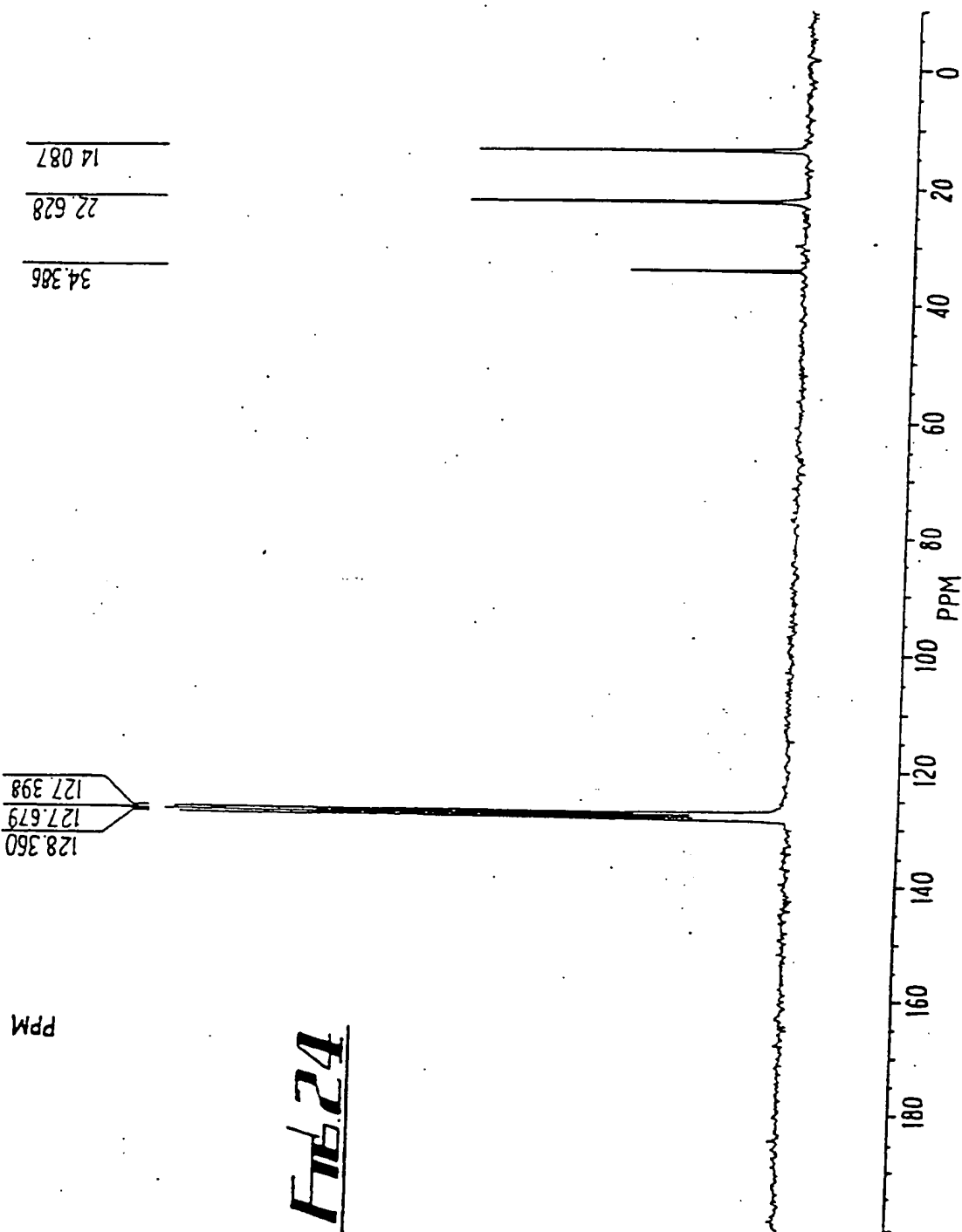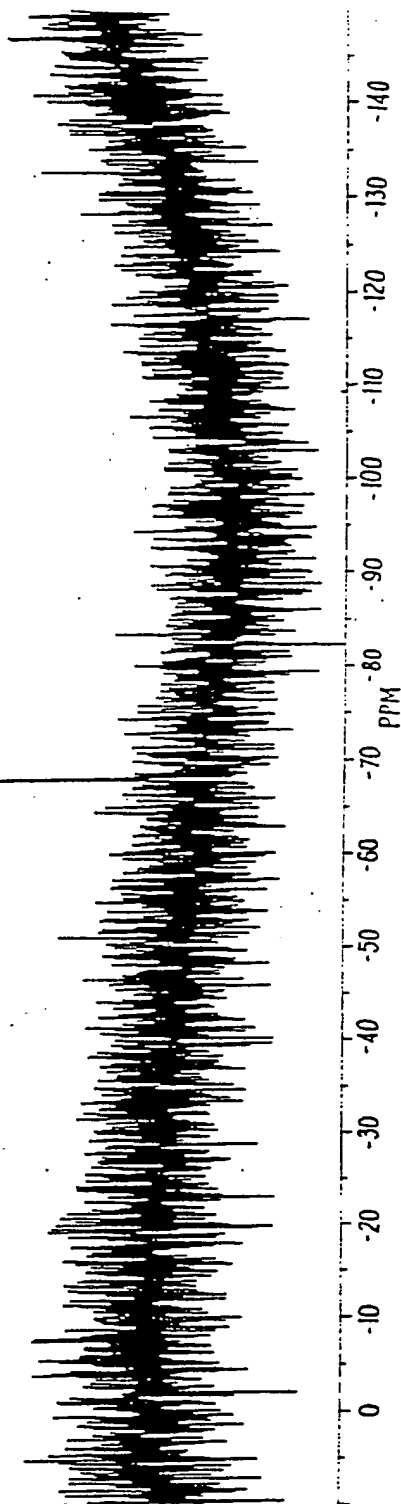
Fig. 25

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5   G03F7/004   C23C16/18   H01L21/285   G03F1/08   G03F7/16
        G03F7/20   C07F1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5   G03F   C23C   H01L   C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,90 02827 (HUGHES AIRCRAFT COMPANY) 22 March 1990	1,2,4; 9-11,16, 18
	see page 8, line 28 - line 36 see page 4, line 13 - line 28	
Y	see page 5, line 1 - line 8 see page 6, line 5 - line 8 see page 10, line 35 - line 36	3,5
X	RESEARCH DISCLOSURE 10 March 1992 , HAVANT, UK page 211 XP000301117 ANONYMOUS 'Pin Repair of MLC Substrate I / O Pads by Focused Ion Beam Techniques' * third paragraph *	1,2,4, 9-11,16, 18
	-/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 February 1994	1 6. 03. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dupart, J-M

Form PCT/ISA/210 (second sheet) (July 1992)

Inter aal Application No
PCT/GB 93/02391

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 714 627 (R.J. PUDDEPHATT ET AL.) 22 December 1987 see column 1, line 8 - line 15 see column 2, line 24 - line 35	1,2, 4-11,13, 16-18
Y	see column 6, line 68 ---	3
X	T. MOLE, E.A. JEFFERY 'ORGANOALUMINIUM COMPOUNDS' 1972 , ELSEVIER PUBLISHING COMPANY , AMSTERDAM, THE NETHERLANDS see page 34 ---	19
X	US,A,5 104 684 (T.TAO ET AL.) 14 April 1992 see column 2, line 13 - line 15 see column 4, line 28 - line 35 see column 4, line 49 - line 68; claims 1,4,6,7 ---	12,13
Y	WO,A,90 06315 (MERCK GMBH) 14 June 1990 see page 14, line 9 - line 16 -----	5

3

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9002827	22-03-90	US-A-	4888204	19-12-89
		EP-A-	0386225	12-09-90
		JP-T-	3501274	22-03-91
US-A-4714627	22-12-87	CA-A-	1250309	21-02-89
US-A-5104684	14-04-92	NONE		
WO-A-9006315	14-06-90	DE-A-	3841643	13-06-90
		EP-A-	0399021	28-11-90
		JP-T-	3502457	06-06-91
		US-A-	5099044	24-03-92